

# PATENT ABSTRACTS OF JAPAN

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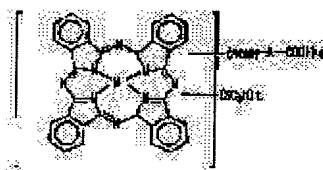
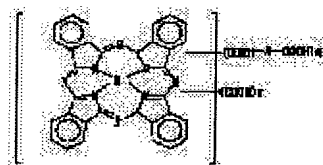
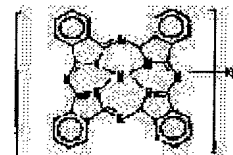
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## (54) RECORDING LIQUID AND RECORDING METHOD USING THE LIQUID

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a recording liquid having excellent cyan color tone and compatibilized color reproducibility, water-resistance and light-resistance of the recorded image by using a phthalocyanine compound in combination with a phthalocyanine compound having free acid form and containing carboxylic acid group introduced into the compound as coloring agents.

**SOLUTION:** This recording liquid contains (A) coloring agents consisting of at least one kind of compound selected from a phthalocyanine compound of formula I (M is H, Cu, Fe, Co or Ni; X is a halogen; (p) is an integer of 0-8) and a halogen-substituted phthalocyanine compound and at least one kind of compound selected from a phthalocyanine compound having free acid form, containing carboxylic acid group and expressed by formula II (A is phenylene, etc.; (q) is an integer of 0-4; (r) is an integer of 0-8; (q) and (r) are not 0 at the same time) or formula III ((s) is an integer of 0-4; (t) is an integer of 0-4; (s) and (t) are not 0 at the same time) and (B) a dispersing agent containing a polymer compound and/or a  $\geq 5$ C surfactant having hydrophilic part and hydrophobic part.

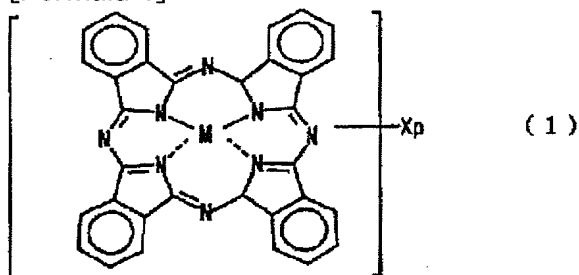


## CLAIMS

[Claim(s)]

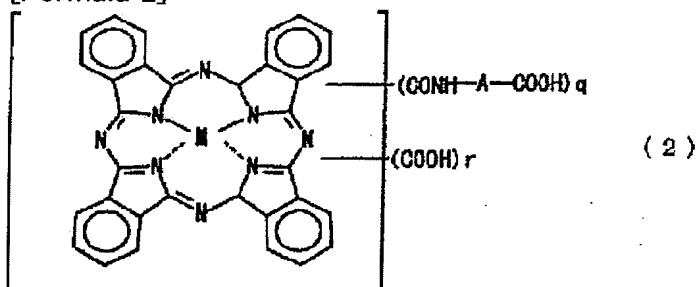
[Claim 1] In the recording ink which uses as a principal component the coloring agent, the water, and the wetting agent which distribute or dissolve in water As a coloring agent At least one sort of the phthalocyanine compound with which the carboxylic-acid radical shown with the free-acid mold expressed with at least one sort and the following general formula (2) of the phthalocyanine compound expressed with the following general formula (1) and a halogenation phthalocyanine compound, or (3) was introduced is contained in coincidence. Recording ink characterized by containing the surfactant which has the high molecular compound which had a hydrophilic part and a hydrophobic part as a dispersant, and/or a with a carbon numbers of five or more alkyl group.

[Formula 1]



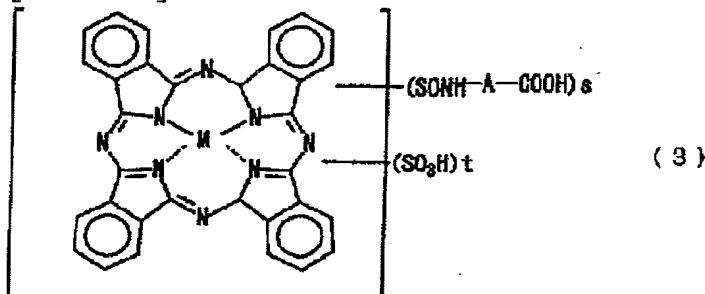
(M expresses a hydrogen atom, and Cu, Fe, Co and nickel among a formula.) X expresses a halogen atom and p expresses the integer of 0 to 8.

[Formula 2]



(M expresses a hydrogen atom, and Cu, Fe, Co and nickel among a formula, and A expresses a phenylene group and a with a carbon numbers of one or more which may branch alkylene group.) q expresses the integer of 0 to 4, r expresses the integer of 0 to 8, and q and r are not set to 0 to coincidence.

[Formula 3]

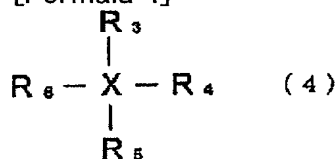


(M expresses a hydrogen atom, and Cu, Fe, Co and nickel among a formula, and A expresses a phenylene group and a with a carbon numbers of one or more which may branch alkylene group.) s expresses the integer of 0 to 4, t expresses the integer of 0

to 4, and s and t are not set to 0 to coincidence.

[Claim 2] Recording ink according to claim 1 characterized by for the particle diameter in the recording ink of the phthalocyanine compound expressed with a general formula (1) being 0.01 micrometers thru/or 0.1 micrometers, and the counter ion of the phthalocyanine compound expressed with a general formula (2) or (3) being sodium, a lithium or the 4th class ammonium expressed with the following general formula (4), the 4th class phosphonium, or alkanolamine ion.

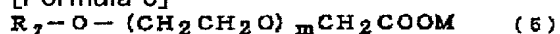
[Formula 4]



(X expresses a nitrogen atom or a phosphorus atom among a formula, and R3, R4, R5, and R6 express a hydrogen atom, a carbon number 1 or the alkyl group of 4, a hydroxyalkyl radical, and an alkyl halide radical.)

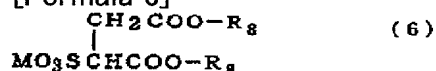
[Claim 3] Recording ink according to claim 1 or 2 which contains the dialkyl sulfo succinate expressed with the polyoxyethylene-alkyl-ether acetate and/or the following general formula (6) which are expressed with the following general formula (5) as a surface active agent, and is characterized by surface tension being 50 or less mN/m.

[Formula 5]



(R7 expresses among a formula the alkyl group to which a carbon number 6 thru/or 14 may branch, and M expresses alkali-metal ion, the 4th class ammonium, the 4th class phosphonium, or alkanolamine.) m expresses the integer of 3 to 12.

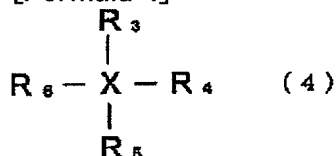
[Formula 6]



(R8 expresses among a formula the alkyl group to which a carbon number 5 thru/or 7 branched, and M expresses alkali-metal ion, the 4th class ammonium, the 4th class phosphonium, or alkanolamine.)

[Claim 4] Recording ink according to claim 3 characterized by the counter ion of the compound expressed with a general formula (5) or (6) being sodium, a lithium or the 4th class ammonium expressed with the following general formula (4), the 4th class phosphonium, or alkanolamine ion.

[Formula 4]



(X expresses a nitrogen atom or a phosphorus atom among a formula, and R3, R4, R5, and R6 express a hydrogen atom, a carbon number 1 or the alkyl group of 4, a hydroxyalkyl radical, and an alkyl halide radical.)

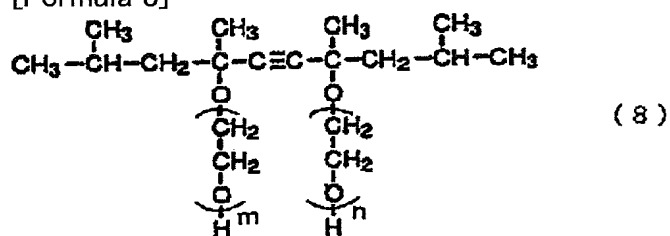
[Claim 5] Recording ink according to claim 1, 2, or 3 which contains the surfactant expressed with the following general formula (7) or a chemical formula (8), and is characterized by surface tension being 50 or less mN/m.

[Formula 7]



(R expresses among a formula the carbon number 6 which may branch thru/or the chain of 14, and k expresses the integer of 5 to 12.)

[Formula 8]



(n expresses the integer of m and 0 to 20 among a formula.)

[Claim 6] Recording ink according to claim 5 characterized by furthermore containing a urea and a urea derivative.

[Claim 7] claims 1, 2, 3, 4, 5, or 6 characterized by containing at least one sort of a pyrrolidone derivative as a wetting agent — the recording ink of any or a publication.

[Claim 8] claims 1, 2, 3, 4, 5, 6, or 7 to which pH is characterized by or more 6 being 11 or less — the recording ink of any or a publication.

[Claim 9] The record approach characterized by making claim 1 thru/or the recording ink of 8 fly as a minute drop with heat energy or mechanical energy, and Stockigt sizing degree forming the image beyond resolution 10 dot/mm x 10 dot/mm 20 pl(s)/mm in recording ink at the record form for 3 seconds or more 2 thru/or by making it adhere two times 200 pl(s)/mm.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the recording ink suitable for especially ink jet record, and the recording ink for ink jet record in which the property which was further excellent especially as an object for color picture formation to the so-called regular paper is shown about the recording ink suitable for using for ink jet record, aqueous writing materials, a recorder, or a pen plotter. \*\*\*\* and this invention relate to the record approach which used the recording ink.

[0002]

[Description of the Prior Art] In recent years, an ink jet printer spreads from advantages, such as low noise and a low running cost, and the color printer printable in a regular paper is also supplied to the commercial scene. In such an ink jet printer The color reproduction nature of a color picture, the water resisting property of an image and lightfastness, drying [ of an image ], Although it is required to satisfy image blot prevention, regurgitation dependability, etc., and amelioration of the color and pigment which are used for the recording ink for ink jet printers is performed in order to usually reconcile the color reproduction nature of a color picture, lightfastness, and a water resisting property in the paper It was difficult to obtain the recording ink which the lightfastness of a record image and a water resisting property were raised, and raised regurgitation dependability, and was moreover excellent in color reproduction nature. For example, although it improves compared with the phthalocyanine system color which introduced the sulfonic group, although the recording ink using the copper-phthalocyanine system color which introduced the carboxylic-acid radical is indicated by JP,63-210175,A, JP,1-126381,A, or JP,1-19077,A as recording ink of a cyanogen color, in order to carry out tenebrescence of the water resisting property by light, it is difficult [ water resisting property / its lightfastness is inadequate, and ] to use it for the poster exposed to daylight for a long period of time. Moreover, in order to acquire the water resisting property of a record image, and lightfastness, various things for which a pigment is used are also tried, but since a problem is in a color tone, it is not adopted except the large-sized plotter with which especially the present condition requires lightfastness. Moreover, when a pigment is used, blinding occurs with the ink jet printer corresponding to high-resolution-izing of a record image etc., and there is also a problem that regurgitation dependability is missing.

[0003] A color tone is improved and the color reproduction nature of a color picture is raised. Then, moreover, the lightfastness of an image, Although the recording ink with which to mix and use a pigment and a color is tried, for example, it mainly becomes JP,60-45668,B from a water-soluble blue color, a blue pigment, and a macromolecule dispersant and water is indicated in order to improve a water resisting property and regurgitation dependability The lightfastness of a color and a water resisting property were inadequate, and neither the permeability of the recording ink to a regular paper nor color enhancement was necessarily enough.

[0004] On the other hand, when forming a color picture with formation of a color picture, especially an ink jet printer, even if a clear image is formed in yellow, a Magenta, and the monochrome printing section of cyanogen, there is a fault that the clear nature of an image falls that it is easy to generate a blot on red, Green, blue 2 color pile part, and its color boundary.

[0005] Since it is raising drying [ of a record image ] by raising the permeability of the recording ink to the recording paper like JP,55-29546,A when drying the record image by ink jet record without using especially an anchorage device, a blot of an image becomes remarkable with the recording paper to be used, and there is a fault that the clear nature of an image falls.

[0006] Although lessening the fall of the clear nature of an image is indicated while raising drying [ of the record image by ink jet record ] by making JP,60-23793,B contain dialkyl sulfo succinate as a surface active agent in recording ink With the recording paper to be used, there is fault that the diameter of a pixel is remarkable, the fall of difference image concentration is also remarkable, and the clear nature of an image falls. Moreover, a surfactant decomposes [ recording ink ] by the alkali side, since the effectiveness of a surfactant is lost and the wettability to the recording paper falls during preservation of recording ink, drying [ of an image ] changes and there is a fault that image degradation on a color boundary occurs.

[0007] Furthermore, although raising drying [ of the record image by ink jet record ] by making recording ink contain the strong base nature matter is indicated by JP,56-57862,A Although it is effective in raising drying when an image is formed in the acid paper by which rosin size was carried out, the effectiveness of the improvement in drying is not seen with the recording paper using the alkyl ketene dimer or the alkenyl sulfo succinic acid as a sizing compound. Moreover, acid paper also has the fault that the effectiveness of the improvement in drying is not seen, in 2 color pile parts in a record image. Moreover, JP,1-203483,A is made to contain a polyhydric-alcohol derivative and pectin in recording ink, and although preventing a blot of a record image by the pectin as a thickener is indicated, since pectin is a nonionic compound which makes a hydroxyl group a hydrophilic group, it has the fault that the regurgitation dependability after a printing pause is missing.

[0008]

[Problem(s) to be Solved by the Invention] In the former, it had the good color tone, and excelled in the color reproduction nature of a color picture, the water resisting property of a record image and lightfastness were enough, and it was difficult to obtain recording ink with the still higher regurgitation dependability in ink jet record.

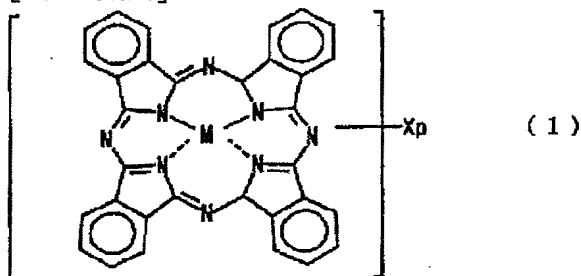
Furthermore, it was difficult to obtain the recording ink which it excels in drying [ of the record image formed in the regular paper ], and a blot of an image is prevented, and can form a clear image. Then, it is in offering the recording ink which the 1st technical problem of this invention solved such a trouble, and has a color tone good especially as a cyanogen color, and was excellent in the color reproduction nature of a color picture, and was excellent in the water resisting property of a record image, and lightfastness. It is in offering the recording ink which can form the image which was excellent in blue and the color reproduction nature of Green, and excelled [ sheet / for over head projectors / transparency ] in transparency especially. It excels in drying [ of the record image formed in the regular paper ], and a blot of an image is prevented, and the 2nd technical problem of this invention is to offer the recording ink which can form a clear image. The 3rd technical problem of this invention is excellent in preservation stability, and is also in after prolonged preservation to offer recording ink with the high regurgitation dependability in ink jet record. Moreover, the 4th technical problem of this invention is to offer recording ink excellent in the regurgitation dependability after the printing pause in ink jet record. Furthermore, the 5th technical problem of this invention is excellent in a water resisting property and lightfastness, and its color reproduction nature is good and it is to offer the ink jet record approach which can form the color picture excellent in clear nature with high resolution.

[0009]

[Means for Solving the Problem] In the recording ink which uses as a principal component the coloring agent, the water, and the wetting agent which distribute or dissolve the above-mentioned technical problem of this invention in water As a coloring agent At least one sort of the phthalic SHININ compound with which the carboxylic-acid radical shown with the free-acid mold expressed with at least one sort and the following general formula (2) of the phthalocyanine compound expressed with

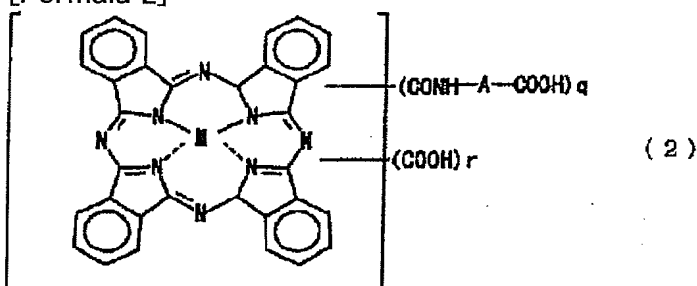
the following general formula (1) and a halogenation phthalocyanine compound, or (3) was introduced is contained in coincidence. It is attained by the recording ink characterized by containing the surfactant which has the high molecular compound which had a hydrophilic part and a hydrophobic part as a dispersant, and/or a with a carbon numbers of five or more alkyl group.

[Formula 1]



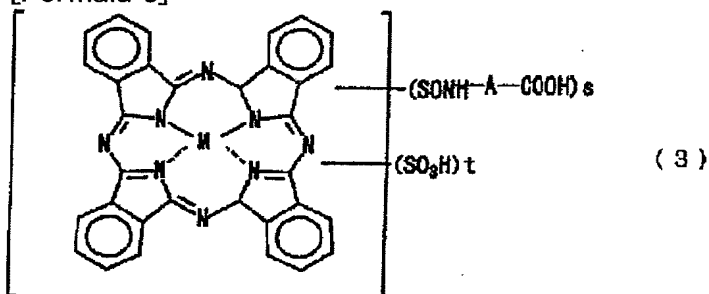
(M expresses a hydrogen atom, and Cu, Fe, Co and nickel among a formula.) X expresses a halogen atom and p expresses the integer of 0 to 8.

[Formula 2]



(M expresses a hydrogen atom, and Cu, Fe, Co and nickel among a formula, and A expresses a phenylene group and a with a carbon numbers of one or more which may branch alkylene group.) q expresses the integer of 0 to 4, r expresses the integer of 0 to 8, and q and r are not set to 0 to coincidence.

[Formula 3]



(M expresses a hydrogen atom, and Cu, Fe, Co and nickel among a formula, and A expresses a phenylene group and a with a carbon numbers of one or more which may branch alkylene group.) s expresses the integer of 0 to 4, t expresses the integer of 0 to 4, and s and t are not set to 0 to coincidence.

[0010] The recording ink which has a color tone good as a cyanogen color, and was excellent in the color reproduction nature of a color picture, and was excellent in the water resisting property of a record image and lightfastness can be obtained by using for coincidence at least one sort of the phthalocyanine compound with which the carboxylic-acid radical shown with the free-acid mold expressed with at least one sort and general formula (2) of the phthalocyanine compound expressed with a general formula (1), or (3) was introduced as a coloring agent. Especially, according to this

recording ink, the image which could form the image excellent in blue and the color reproduction nature of Green, and excelled [ sheet / for over head projectors / transparence ] in transparency can be formed.

[0011] Although a hue and saturation are inadequate and inferior to the color reproduction nature of a color picture if independent even if it atomizes it when the phthalocyanine compound expressed with a general formula (1) is used as a coloring agent, this By using with at least one sort of the phthalocyanine compound with which the carboxylic-acid radical shown with the free-acid mold expressed with a general formula (2) or (3) was introduced It is because adjustment of a hue and improvement in saturation can be aimed at and these phthalocyanine compounds are excellent in a water resisting property and lightfastness. Moreover, by making the surfactant which has the high molecular compound which had a hydrophilic part and a hydrophobic part as a dispersant, and/or a with a carbon numbers of five or more alkyl group contain, the permeability over the recording papers, such as a regular paper of recording ink, can be raised, and drying [ of a record image ] can be raised, and a blot of an image can be prevented, and a clear image can be formed.

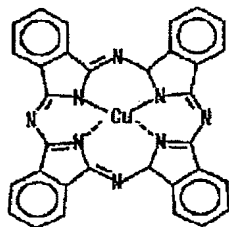
[0012] as an example of a phthalocyanine compound expressed with the general formula (1) in this invention, (2), or (3), \*\* can be mentioned to Table 1, 2, or 3, respectively.

[0013]

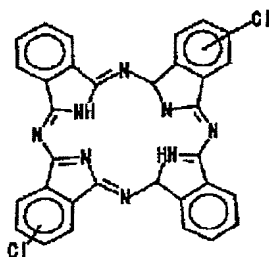
[Table 1]



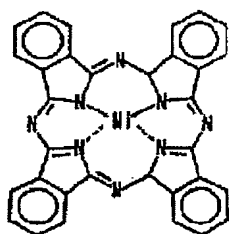
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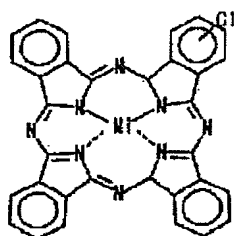
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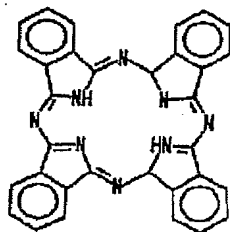
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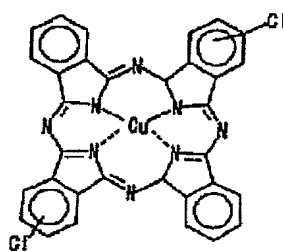
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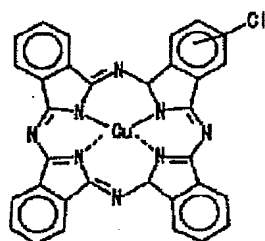
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(1-7)



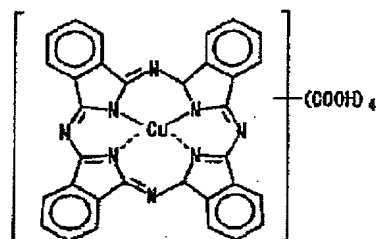
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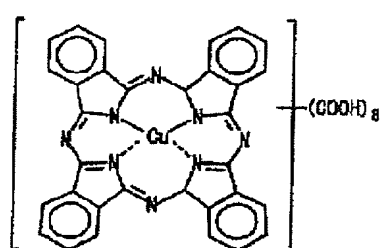
[0014]

[Table 2]

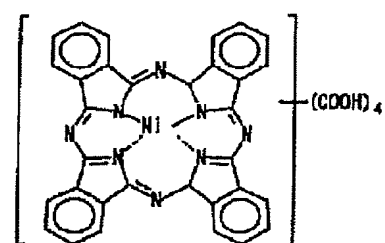
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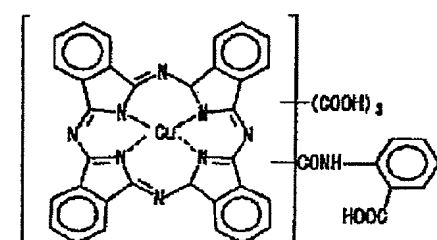
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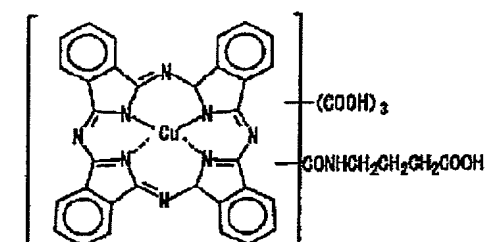
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(2-4)

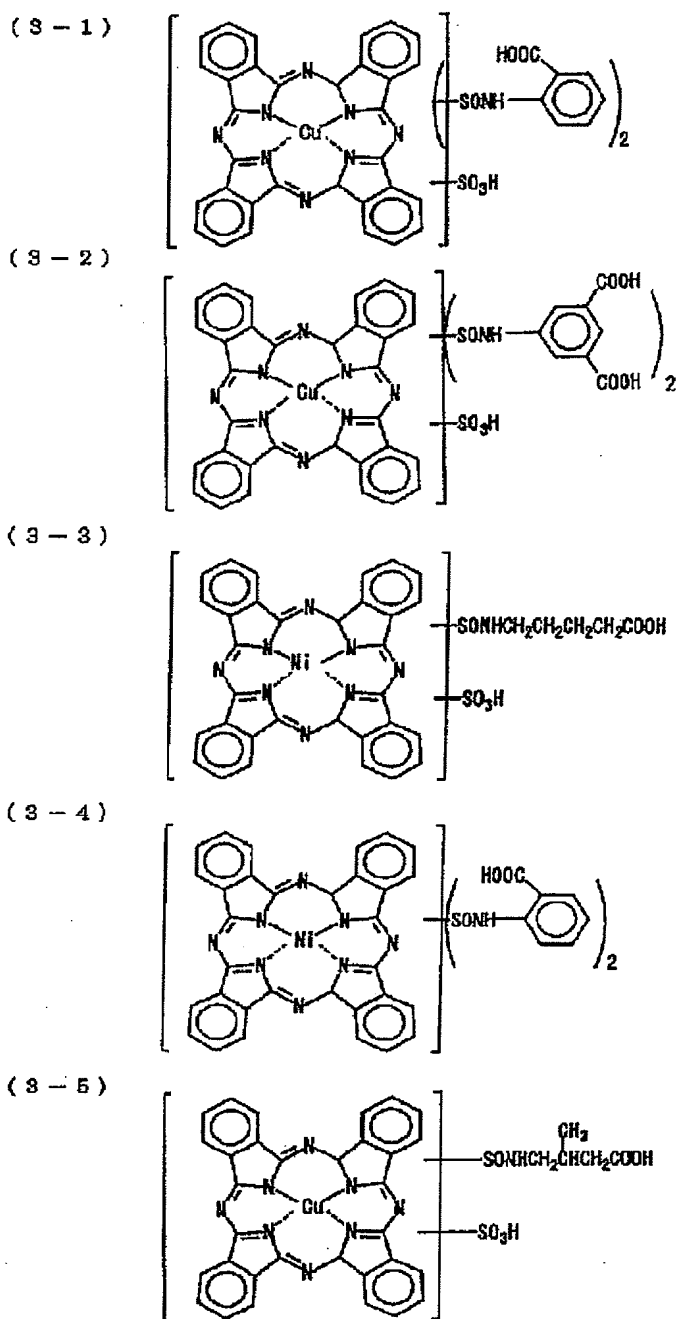


(2-5)



[0015]

[Table 3]

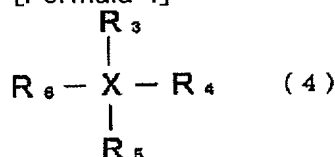


[0016] In addition, as for these phthalocyanine compounds, it is desirable to contain polyvalent metal ion, chloride ion, sulfate ion, etc. as an impurity in a synthetic phase, and for ion exchange resin, a reverse osmotic membrane, an ultrafiltration, etc. to refine, and to use. By refining and using, the blinding of a nozzle can be prevented in an ink jet printer.

[0017] The phthalocyanine compound expressed with a general formula (1) is atomized and used, and its 0.01–0.1 micrometers are desirable as particle diameter in the recording ink. Moreover, the dissolution stability of a phthalocyanine compound expressed with a general formula (2) or (3) can be raised by using the counter ion of the phthalocyanine compound expressed with a general formula (2) or (3) as sodium, a lithium or the 4th class ammonium expressed with the following general formula (4), the 4th class phosphonium, or alkanolamine ion.

[0018]

[Formula 4]



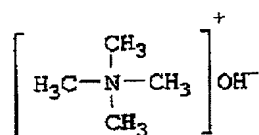
(X expresses a nitrogen atom or a phosphorus atom among a formula, and R3, R4, R5, and R6 express a hydrogen atom, a carbon number 1 or the alkyl group of 4, a hydroxyalkyl radical, and an alkyl halide radical.)

What is necessary is just to add the hydroxide shown in a sodium hydroxide, a lithium hydroxide, or the following table 4 to recording ink, in order to carry out the counter ion of the phthalocyanine compound expressed with a general formula (2) or (3) in this way.

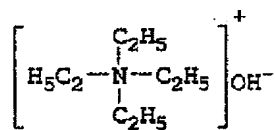
[0019]

[Table 4]

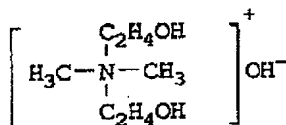
(4-1)



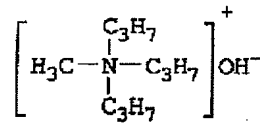
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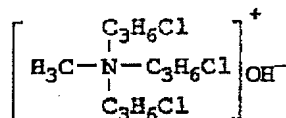
(4-3)



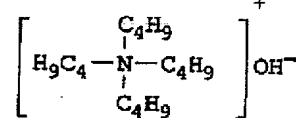
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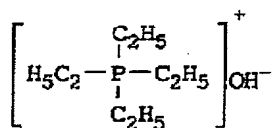
(4-5)



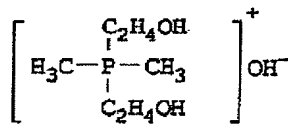
(4-6)



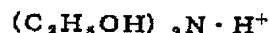
(4-7)



(4-8)



(4-9)



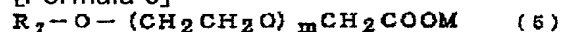
[0020] As mentioned above, the particle diameter in the recording ink of the phthalocyanine compound particle expressed with a general formula (1) is set to 0.01–0.1 micrometers. The counter ion of the phthalocyanine compound expressed with a general formula (2) or (3) Moreover, sodium, By considering as a lithium or the 4th class ammonium expressed with said general formula (4), the 4th class phosphonium, or alkanolamine ion When the preservation stability of recording ink can be raised and recording ink is used as an object for ink jet printers, blinding of a nozzle is not generated and record with high regurgitation dependability can be performed.

[0021] Next, the dispersant used in this invention is explained. The dialkyl sulfo succinate expressed with the polyoxyethylene-alkyl-ether acetate or the following

general formula (6) expressed with the following general formula (5) which is an anion system surfactant as a surfactant which has a carbon numbers of five or more alkyl group is desirable.

[0022]

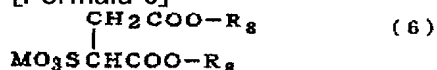
[Formula 5]



(R7 expresses among a formula the alkyl group to which a carbon number 6 thru/or 14 may branch, and M expresses alkali-metal ion, the 4th class ammonium, the 4th class phosphonium, or alkanolamine.) m expresses the integer of 3 to 12.

[0023]

[Formula 6]



(R8 expresses among a formula the alkyl group to which a carbon number 5 thru/or 7 branched, and M expresses alkali-metal ion, the 4th class ammonium, the 4th class phosphonium, or alkanolamine.)

[0024] By using these anion system surfactants, the image which the permeability of the recording ink to the recording papers, such as a regular paper, was raised, and drying [ of a record image ] was raised, and prevented the blot of an image, and was excellent in clear nature can be formed. The image which the wettability on recording ink and front faces of the recording paper, such as a regular paper, could be raised more, the permeability of the recording ink to the recording paper was raised, and drying [ of a record image ] was raised, and prevented the blot of an image, and was excellent in clear nature can be formed by making more preferably 50 or less mN/m of surface tension of recording ink into 40 or less mN/m especially using these surfactants.

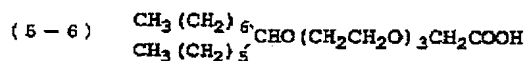
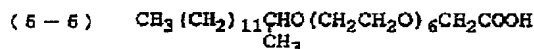
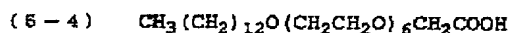
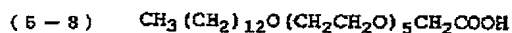
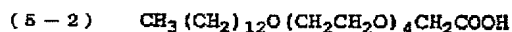
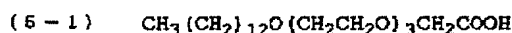
[0025] The surface tension in this invention is an index which shows the permeability to the recording paper of recording ink, especially surface formation is carried out, and shows the dynamic surface tension in the short time amount for 1 or less second, and differs from the static surface tension measured by saturation time. Although all can be used if it is the approach of measuring the dynamic surface tension for 1 or less second conventionally by the well-known approach indicated by JP,63-31237,A etc. as a measuring method, the value which the Wilhelmy type hung here and was measured using the plate type surface tension balance is shown.

[0026] In addition, by using the above-mentioned anion system surfactant, recording ink thickens that the image which prevented the blot of an image and was excellent in clear nature can be formed by the proton supplied from recording paper front faces, such as a regular paper, and, thereby, it is presumed for a blot to decrease.

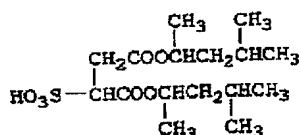
[0027] The example of dialkyl sulfo succinate expressed with the polyoxyethylene-alkyl-ether acetate or the general formula (6) expressed with a general formula (5) is shown in the following table 5 with a free-acid mold.

[0028]

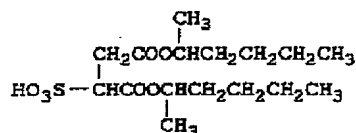
[Table 5]



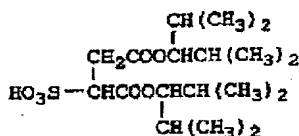
(6-1)



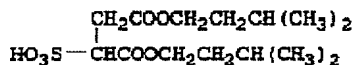
(6-2)



(6-3)



(6-4)



[0029] As counter ion [ of dialkyl sulfo succinate ] M expressed with the polyoxyethylene-alkyl-ether acetate or the general formula (6) expressed with a general formula (5), sodium, a lithium or the 4th class ammonium expressed with said general formula (4), the 4th class phosphonium, or especially alkanolamine ion is desirable. By making counter ion M into this appearance, the dissolution stability of these anion system surfactant can be raised more, and the recording ink which was excellent with preservation stability can be obtained. After this saves recording ink for a long period of time, record with high regurgitation dependability can be performed in ink jet record. What is necessary is just to add the hydroxide shown in a sodium hydroxide, a lithium hydroxide, or said table 4 to recording ink, in order to carry out counter ion M in this way.

[0030] As a content in the recording ink of the dialkyl sulfo succinate expressed with the polyoxyethylene-alkyl-ether acetate or the general formula (6) expressed with a general formula (5), 0.05 - 10 % of the weight is desirable. The permeability over the recording paper required of ink jet record in the range of this content can be given to recording ink. If it becomes less than 0.05 % of the weight, the blot by the boundary of 2 color pile sections will occur, if 10 % of the weight is exceeded, the FUTAROSHININ compound which the anion system surfactant itself expressed with a general formula (5) or (6) becomes easy to deposit at low temperature, and is expressed with a general formula (2) or (3) may deposit, and the regurgitation dependability in IKUJIETTO record will come to fall.

[0031] In addition, the counter ion of the phthalocyanine compound expressed with a general formula (2) or (3) in the recording ink of this invention as mentioned above, Counter ion M of an anion system surfactant expressed with a general formula (5) or (6) Or sodium, Although the dissolution stability of these phthalocyanines compound or an anion system surfactant can be raised by considering as a lithium or the 4th class ammonium expressed with said general formula (4), the 4th class phosphonium, or an alkanolamine cation All do not need to be the 4th class ammonium and the 4th class

phosphonium which are expressed with sodium, a lithium, or said general formula (4), or alkanolamine ion, and a counter ion can also consider as mixing with other alkali ion. As an amount of the 4th class ammonium and the 4th class phosphonium which are expressed with sodium, a lithium, or said general formula (4), or alkanolamine ion, 30% or more is desirable to the number of mols of the phthalocyanine compound expressed with a general formula (2) or (3), and an anion system surfactant, and especially 50% or more is desirable.

[0032] Moreover, the acetylene glycol system surfactant expressed with the polyoxyethylene alkyl phenyl ether or the following general formula (8) expressed with the following general formula (7) which is a non-ion system surfactant as a surfactant which has a with a carbon numbers of five or more alkyl group is also desirable.

[0033]

[Formula 7]

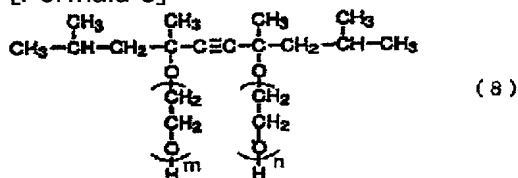


(R expresses among a formula the carbon number 6 which may branch thru/or the chain of 14, and k expresses the integer of 5 to 12.)

An alkyl group, an alkenyl radical, etc. are mentioned as a chain.

[0034]

[Formula 8]



(n expresses the integer of m and 0 to 20 among a formula.)

[0035] By using these non-ion system surfactants, the image which the permeability of the recording ink to the recording papers, such as a regular paper, was raised, and drying [ of a record image ] was raised, and prevented the blot of an image, and was excellent in clear nature can be formed. The image which the wettability on recording ink and front faces of the recording paper, such as a regular paper, could be raised more, the permeability of the recording ink to the recording paper was raised, and drying [ of a record image ] was raised, and prevented the blot of an image, and was excellent in clear nature can be formed by making surface tension of recording ink into 50 or less mN/m especially using these non-ion system surfactants. Furthermore, by using urea derivatives, such as a urea, a hydroxyethyl urea, or a dihydroxyethyl urea, with a non-[ these ] ion system surface active agent, permeability can be raised by weakening the interaction between the phtalo SHININ compounds and non-ion system surface active agents which are expressed with said general formula (1), (2), or (3), and easing a meeting of a phtalo SHININ compound, and the regurgitation dependability and the mothball nature of recording ink in ink jet record can be improved. As an addition of these ureas or a urea derivative, 0.1 – 5 % of the weight is desirable. If fewer than 0.1 % of the weight, it is ineffective, and when 5 % of the weight is exceeded, I may \*\*\*\* effect to the viscosity change at the time of moisture evaporation, and regurgitation dependability may be spoiled.

[0036] furthermore, using the high molecular compound which has a hydrophilic part and a hydrophobic part as a pigment agent as a high molecular compound which is desirable and has such a hydrophilic part and a hydrophobic part As a hydrophilic giant molecule, for example, by the natural system, gum arabic, TORAGANGAMU, Good AGAMU, karaya gum, locust bean gum, arabino GARAKUTON, Vegetable macromolecules, such as pectin and KUINSU seed starch, an alginic acid, Seaweed

system giant molecules, such as a carrageenan and an agar, gelatin, casein, albumin, Microorganism system giant molecules, such as animal system giant molecules, such as a collagen, xanthene gum, and a dextran, \*\*\*\* is mentioned. By the semisynthesis system Methyl cellulose, ethyl cellulose, Fibrin system macromolecules, such as hydroxyethyl cellulose, hydroxypropylcellulose, and force RUBOKISHI methyl cellulose, Seaweed system macromolecules, such as starch system macromolecules, such as sodium carboxymethyl starch and sodium starch phosphate, sodium alginate, and propylene glycol alginate, etc. are mentioned. Moreover, by the pure composition system, the high molecular compound which has the salt of cationic functional groups, such as acrylic resin, such as vinyl system macromolecules, such as polyvinyl alcohol, a polyvinyl pyrrolidone, and polyvinyl methyl ether, polyacrylamide non-constructing a bridge, polyacrylic acid and its alkali-metal salt, and water-soluble styrene acrylic resin, water-soluble styrene maleic resin, water-soluble vinyl naphthalene acrylic resin, water-soluble vinyl naphthalene maleic resin, an alkali-metal salt of 8-naphthalene sulfonic-acid formalin condensate, the fourth class ammonium, and an amino group, in a side chain is mentioned. Moreover, naturally-occurring-polymers compounds, such as a shellac, can also be used.

[0037] Although many above-mentioned components are distributed or dissolved in water, in order that the recording ink of this invention may prevent the desiccation at the time of storage of recording ink further, it is the purpose for raising the dissolution stability of a phthalo SHININ compound expressed with a general formula (2) or (3) etc., and the water-soluble organic solvent is added by the recording ink of this invention as a wetting agent.

[0038] As such a water-soluble organic solvent, for example Ethylene glycol, A diethylene glycol, triethylene glycol, a polyethylene glycol, A polypropylene glycol, 1,5-pentanediol, 1, 6 hexandiol, Glycerol, 1 and 2, 6-hexane trio-RU, 1 and 2, 4-butane triol, Polyhydric alcohol, such as 1, 2, 3-butane triol, and PETORI oar Ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, The diethylene-glycol monomethyl ether, diethylene glycol monoethyl ether, The diethylene-glycol monobutyl ether, the tetraethylene glycol monomethyl ether, Polyhydric-alcohol alkyl ether, such as the propylene glycol monoethyl ether Polyhydric-alcohol aryl ether, such as ethylene glycol monophenyl ether and ethylene glycol mono-benzyl ether, A N-methyl-2-pyrrolidone, an N-hydroxyethyl-2-pyrrolidone, Nitrogen-containing heterocyclic compounds, such as 2-pyrrolidone, 1, 3-dimethyl imidazolidinone, and epsilon caprolactam, Amides, such as a formamide, N-methyl formamide, and N,N-dimethylformamide Monoethanolamine, diethanolamine, triethanolamine, Amines, such as a monoethyl amine, diethylamine, and triethylamine, sulphur-containing compounds, such as dimethyl sulfoxide, a sulfolane, and thiodiethanol, propylene carbonate, ethylene carbonate, gamma-butyrolactone, etc. can be illustrated, and these water-soluble organic solvents are independent — or more than one can be mixed and it can use.

[0039] In these especially a water-soluble desirable organic solvent A diethylene glycol, Thiodiethanol, polyethylene glycols 200-600, triethylene glycol, Glycerol, 1 and 2, 6-hexane triol, 1 and 2, 4-butane triol, PETORI oar, 1,5-pentanediol, a N-methyl-2-pyrrolidone, It is N-hydroxyethyl-2-pyrrolidone, 2-pyrrolidone, 1, and 3-dimethyl imidazolidinone etc. While raising the dissolution stability of a phthalo SHININ compound expressed with a general formula (2) or (3) by using these water-soluble organic solvents, moisture evaporation can be controlled and desiccation of recording ink can be prevented. When prolonged printing is stopped [ and ] after saving recording ink for a long period of time, ink jet record excellent in regurgitation dependability can be performed. Moreover, when pyrrolidone derivatives, such as an N-hydroxyethyl-2-pyrrolidone, are especially added to recording ink, the distributed stability of a phthalocyanine compound particle expressed with said general formula (1) can be



raised, and the preservation stability of recording ink can be raised further. After this saves recording ink for a long period of time, in ink jet record, ink jet record with still higher regurgitation dependability can be performed.

[0040] In order to adjust surface tension to the recording ink of this invention Moreover, said general formula (5), In addition to the surface active agent expressed with (6), (7), or (8), the diethylene-glycol monophenyl ether, The ethylene glycol mono-fail ether, ethylene glycol monoallyl ether, The diethylene-glycol monophenyl ether, the diethylene-glycol monobutyl ether, Alkyl or aryl ether of polyhydric alcohol, such as the propylene glycol monobutyl ether and the tetraethylene glycol chlorophenyl ether, Lower alcohol, such as a polyoxyethylene polyoxypropylene block copolymer, a fluorochemical surfactant or ethanol, and 2-propanol, can be added, and especially the diethylene-glycol monobutyl ether is desirable.

[0041] At least one sort of a phtalo SHININ compound expressed with at least one sort and said general formula (2) of the phthalocyanine compound expressed with said general formula (1), or (3) as a coloring matter of this invention is used for coincidence, and also other coloring agents can be mixed and used if needed. The thing a water resisting property and lightfastness excelled [ thing ] in the water soluble dye classified into acid dye, a substantivity color, basic dye, reactive dye, and the food color in a Color Index as such a coloring agent, or a pigment is used. As for these, it is desirable to add in the range in which neither a water resisting property nor lightfastness is alienated.

[0042] If these colors are mentioned concretely, as acid dye and the food color C. The I. acid yellow 17, 23, 42, 44, and 79,142, C.I. acid red 1, 8, 13, 14, 18, 26, 27, 35, 37, 42, 52, 82, 87, 89, 92, 97, 106, 111, 114, 115, 134, 186, 249, and 254, As 289, the C.I. acid blues 9, 29, 45, and 92,249, the C.I. acid blacks 1, 2, 7, 24, 26, and 94, the C.I. hood yellow 3 and 4, the C.I. hood red 7, 9, and 14, the C.I. hood blacks 1 and 2, and a substantivity color C. The I. direct yellow 1, 12, 24, 26, 33, 44, 50, and 86,120,132,142,144, C.I. direct red 1, 4, 9, 13, 17, 20, 28, 31, 39, 80, 81, 83, and 89,225,227, C. I. direct Orange 26, 29, and 62,102, the C.I. direct blues 1, 2, 6, 15, 22, 25, 71, 76, 79, 86, 87, 90, and 98,163,165,199,202, C.I. direct blacks 19, 22, 32, 38, 51, and 56, As 71, 74, 75, 77,154,168,171, and basic dye C. I. BASIC yellow 1, 2, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 40, 41, 45, and 49, 51, 53, 63, 64, 65, 67, 70, 73, 77, 87 and 91, C.I. BASIC red 2, 12, and 13, 14, 15, 18, 22, 23, 24, 27, 29, 35, 36, 38, 39, 46, 49, 51, 52, 54, 59, 68, 69, 70, 73, 78, 82,102,104,109,112, the C.I. BASIC blues 1, 3, 5, 7, 9, 21, 22, and 26, As 35, 41, 45, 47, 54, 62, 65, 66, 67, 69, 75, 77, 78, 89,92, 93, 105, 117, 120, 122, 124, 129 and 137,141,147,155, the C.I. BASIC blacks 2 and 8, and reactive dye C. The I. reactive blacks 3, 4, 7, 11, 12, and 17, the C.I. reactive yellow 1, 5, 11, 13, 14, 20, 21, 22, 25, 40, 47, 51, 55, 65, and 67, C.I. reactive red 1, 14, 17, 25, 26, 32, and 37, 44, 46, 55, 60, 66, 74, 79, 96, 97, the C.I. reactive blues 1, 2, 7, 14, 15, 23, 32, 35, 38, 41, 63, and 80, and 95 grades can be used, and especially acid dye and a substantivity color are desirable.

[0043] Moreover, as a pigment, an azo system, a phthalocyanine system, an anthraquinone system, a dioxazine system, an indigo system, a thioindigo system, a perylene system, an iso in DORENON system, aniline black, an azomethine system, a rhodamine B lake pigment, carbon black, etc. are mentioned as an organic pigment, and ferrous oxide, titanium oxide, a calcium carbonate, a barium sulfate, an aluminum hydroxide, barium yellow, Berlin blue, cadmium red, chrome yellow, and a metal powder are mentioned as an inorganic pigment.

[0044] Furthermore, to the recording ink of this invention, the additive known conventionally, for example, a preservation-from-decay antifungal agent, a rusr-proofer, pH regulator, a water-soluble ultraviolet ray absorbent, or a water-soluble infrared absorption agent can be added.

[0045] As a preservation-from-decay antifungal agent, sodium dehydroacetate, sodium

sorbate, 2-pyridine thiol-1-oxide sodium, sodium benzoate, pentachlorophenol sodium, etc. can be used, and an acid sulfite, a sodium thiosulfate, thiodiglycolic acid Amon, a diisopropyl AMMONIUM nit light, pentaerythritol tetranitrate, a dicyclohexyl ammonium nit light, etc. can be used as a rust-proofer.

[0046] The matter of arbitration can be used, if a bad influence can be adjusted to \*\*\*\*\* and pH can be adjusted to the recording ink prepared as a pH regulator six or more. As an example of pH regulator, the carbonate of alkali metal, such as the hydroxide of alkali metals, such as amines, such as diethanolamine and triethanolamine, a lithium hydroxide, a sodium hydroxide, and a potassium hydroxide, ammonium hydroxide, the 4th class ammonium hydroxide, the 4th class phosphonium hydroxide, a lithium carbonate, a sodium carbonate, and potassium carbonate, etc. is mentioned. Moreover, as a chelating reagent, ethylenediaminetetraacetic acid sodium, nitrilotriacetic acid sodium, hydroxyethyl ethylenediamine triacetic-acid sodium, diethylenetriamine pentaacetic acid sodium, URAMIRU sodium diacetate, etc. can be used, for example.

[0047] Even when the preservation stability of recording ink improves by adjusting to 11 especially or less [ 6 or more ] or more by six and pH in the recording ink of this invention is left in recording ink car TORIJI in an ink jet printer etc. for a long period of time, ink jet record can be performed without the blinding of an ink jet nozzle arising. however, since a surfactant decomposes [ pH ] or more by nine at the time of preservation of recording ink when the surfactant expressed with a general formula (6) is used, and change of record liquid nature tends to take place, when using the surfactant expressed with a general formula (6), it is desirable for it to be alike and to adjust pH to 6-9.

[0048] In order to perform ink jet record using the recording ink of this invention Recording ink is made to breathe out with heat energy or mechanical energy from the detailed delivery of for example, the diameter of 20-60 micrometer. By \*\* in which weight makes it fly by the rate 5 - 20 m/s as a drop of 10ng-160ng, Stockigt sizing degree forms the record form for 3 seconds or more in the so-called regular paper for 3 seconds or more, and Stockigt sizing degree forms an image It excels in a water resisting property and lightfastness, and color reproduction nature is good and can form the color picture excellent in clear nature with high resolution. Especially, Stockigt sizing degree can form the image of the high resolution beyond resolution 10 dot/mm x 10 dot/mm in the record form for 3 seconds or more 20 pl(s)/mm in recording ink 2 thru/or by making it adhere two times 200 pl(s)/mm. Moreover, pH has many things of 5-6, and, as for a copy paper, letter paper, etc. which are generally used in office etc., can form the color picture which whose color reproduction nature was good and was excellent in clear nature by excelling in a water resisting property and lightfastness by using the recording ink of this invention for these, and performing ink jet record with high resolution. Moreover, by using the recording ink of this invention, the image which excelled [ sheet / for over head projectors (OHP) / for ink jet record / transparence ] in transparency can be formed, and the color picture which shows coloring which was excellent at the time of OHP projection can be obtained.

[0049]

[Example] An example explains this invention below.

[0050] The ultrasonic homogenizer distributed the compound of example 1 example (1-1) under existence of a dispersant, particle diameter was set to 0.1 micrometers or less, the churning dissolution of the constituent of the following formula was carried out using these dispersion liquid, 10% water solution of lithium hydroxides adjusted so that pH might be set to 8.5, this was filtered with the 0.8-micrometer Teflon filter, and recording ink 1 was obtained.

The compound of an example (1-1) 1.0 % of the weight The compound of an example (2-1) 1.0 % of the weight Styrene acrylic-acid polymer 0.4 % of the weight Glycerol 5

Weight % N-hydroxyethyl pyrrolidone 5 Surface active agent of a weight % example (5-1) 0.8 % of the weight Sodium dehydroacetate 0.2 % of the weight Ion exchange water Residue [0051] Recording ink 2 was prepared like the example 1 using the example 2 following constituent except having adjusted pH to 8.8 by the sodium hydroxide.

The compound of an example (1-1) 1.2 % of the weight The compound of an example (1-4) 0.8 % of the weight The compound of an example (2-2) 0.6 % of the weight 1, 2, 6-hexane triol 4 Weight % 1,5-pentanediol 8 Surfactant of a weight % example (5-1) 1.2 % of the weight 25% water solution of an example (4-1) 0.8 % of the weight Sodium alginate 0.05 % of the weight Urea 5 Weight % 2-pyridine thiol-1-oxide sodium 0.2 % of the weight Ion exchange water Residue [0052] Recording ink 3 was prepared like the example 1 using the example 3 following constituent except the lithium hydroxide having adjusted pH to 8.5.

The compound of an example (1-3) 1 The compound of a weight % example (2-5) 0.5 % of the weight The compound of an example (3-3) 0.5 % of the weight Diethylene glycol 5 Weight % glycerol 5 Weight % styrene acrylic-acid copolymer 0.5 % of the weight It sets to a general formula (7), and R is C<sub>9</sub>H<sub>19</sub> and k is the surfactant of 12. 2 25% water solution of a weight % example (4-3) 0.2 % of the weight Sodium dehydroacetate 0.2 % of the weight Ion exchange water Residue [0053] Recording ink 4 was prepared like the example 1 using the example 4 following constituent except the lithium hydroxide having adjusted pH to 9.5.

The compound of an example (1-3) 1.0 % of the weight The compound of an example (3-1) 1.2 % of the weight Ethylene glycol 5 Weight % glycerol 2 Weight % 1,5-pentanediol 8 Weight % 2-pyrrolidone 2 Weight % polyoxyethylene polyoxyethylene block copolymer 1 The surfactant of a weight % general formula (8) (m, n= 20) 0.8 % of the weight 25% water solution of an example (4-4) 2 Weight % urea 5 Weight % sodium benzoate 0.2 % of the weight Ion exchange water Residue [0054] Recording ink 5 was prepared like the example 1 using the example 5 following constituent except having adjusted pH to 7.8 by the sodium hydroxide.

The compound of an example (1-4) 1.2 % of the weight The compound of an example (2-1) 0.3 % of the weight The compound of an example (3-3) 0.5 % of the weight Triethylene glycol 5 Weight % PETORI oar 10 Weight % N-methyl-2-pyrrolidone 5 The surfactant of a weight % example (6-1) 2 25% water solution of a weight % example (4-2) 1.5 % of the weight Hydroxyethyl urea 5 Weight % 2-pyridine thiol-1-oxide sodium 0.2 % of the weight Ion exchange water Residue [0055] Recording ink 6 was prepared like the example 1 using the example 6 following constituent except the lithium hydroxide having adjusted pH to 8.

The compound of an example (1-3) 1.5 % of the weight The compound of an example (2-5) 1.6 % of the weight 2-pyrrolidone 8 Weight % glycerol 7 The surfactant of a weight % general formula (8) (m+n=15) 1 The surfactant of a weight % general formula (8) (m, n= 0) 1 25% water solution of a weight % example (4-7) 2 % of the weight Hydroxyethyl urea 5 Weight % sodium dehydroacetate 0.2 % of the weight Ion exchange water Residue [0056] Recording ink 7 was prepared like the example 1 using the example 7 following constituent except the lithium hydroxide having adjusted pH to 8.

The compound of an example (1-1) 1.2 % of the weight The compound of an example (1-5) 0.3 % of the weight The compound of an example (3-2) 0.8 % of the weight N-methyl-2-pyrrolidone 8 Weight % 1,5-pentanediol 8 Surfactant of a weight % example (5-4) 0.8 % of the weight Sodium benzoate 0.5 % of the weight Ion exchange water Residue [0057] Recording ink 8 was prepared like the example 1 using the example 8 following constituent except the lithium hydroxide having adjusted pH to 7.5.

The compound of an example (1-1) 1.5 % of the weight The compound of an example (3-1) 1.0 % of the weight C.I. direct blue 199 1.0 % of the weight Thiodiethanol 5 Weight % glycerol 10 It sets to a weight % general formula (7), and R is C<sub>10</sub>H<sub>21</sub> and k is the surfactant of 12. 1.5 % of the weight Sodium benzoate 0.5 % of the weight Ion exchange

water Residue [0058] Recording ink 9 was prepared like the example 1 using the example 9 following constituent except the lithium hydroxide having adjusted pH to 8. The compound of an example (1-1) 1.5 % of the weight The compound of an example (1-4) 1.0 % of the weight The compound of an example (3-1) 0.5 % of the weight 2-pyrrolidone 5.0 % of the weight Glycerol 15.0 % of the weight The surfactant of a general formula (8) ( $m+n=40$ ) 1.0 % of the weight The surfactant of an example (5-2) 1.0 % of the weight Pentachlorophenol sodium 0.2-% of the weight ion exchange water Residue [0059] Recording ink 10 was prepared like the example 1 using the example 10 following constituent except the lithium hydroxide having adjusted pH to 8.

The compound of an example (1-1) 1.0 % of the weight The compound of an example (3-1) 0.8 % of the weight The compound of an example (3-5) 0.2 % of the weight 2-pyrrolidone 5.0 % of the weight Glycerol 15.0 % of the weight The surfactant of a general formula (8) ( $m+n=40$ ) 2.0 % of the weight Surface active agent of an example (5-2) 1.0 % of the weight Sodium dehydroacetate 0.2 % of the weight Ion exchange water Residue [0060] example of comparison 1 example 1 — setting — an example (1-1) — and (2-1) obtained recording ink 11 like the example 1 except having replaced with the compound and having used the C.I. acid blue 249.

[0061] example of comparison 2 example 2 — setting — an example (1-1) — and (1-4) obtained recording ink 12 like the example 2 except having replaced with the compound and having used the C.I. direct blue 199.

[0062] Recording ink 13 was obtained like the example 3 except having set pH of recording ink to 4.5 except for 25% water solution of an example (4-3), the styrene acrylic-acid copolymer, and the surfactant of a general formula (7) in example of comparison 3 example 3.

[0063] Recording ink 14 was obtained like the example 3 except having replaced with the surface active agent of a general formula (7) in example of comparison 4 example 3, and having used the JI (isobutyl) sulfo sodium succinate.

[0064] Recording ink 15 was obtained like the example 1 except having replaced with the compound of an example (3-1) in example of comparison 5 example 4, and having used the C.I. acid blue 1.

[0065] Recording ink 16 was obtained like the example 6 except the potassium hydroxide having adjusted pH to 8 except for the surfactant of the 25% water solution and the general formula (8) of an example (4-7) in example of comparison 6 example 6.

[0066] Recording ink 17 was obtained like the example 1 except having replaced with the compound of an example (2-1) in example of comparison 7 example 1, having replaced the lithium hydroxide with ammonium hydroxide using the C.I. direct blue 25, and having adjusted pH.

[0067] the recording ink obtained next by the above-mentioned examples 1-10 and the examples 1-7 of a comparison — the following — the thing trial [ like ] was performed. The result is shown in Table 6.

1) 45 micrometers of diameters of a nozzle of the clear nature thermal ink jet method of an image, With 33 micrometers of diameters of a nozzle which used the ink jet printer and Laminating PZT which have the nozzle of 300dpi for the pressurization of liquid room passage, and the ink jet printer which has the nozzle of 128 It printed to three kinds of print forms, commercial recycled paper, paper of fine quality, and bond paper, and about the printing image, a blot of 2 color pile sections boundaries, an image blot, a color tone, and concentration were synthetically judged by viewing, and the clear nature of an image was evaluated. In Table 6, the case where x mark is not satisfied in any of three kinds of print forms in the case where it is satisfied with at least one sort of print forms of \*\* mark in the case where O mark is satisfied also in any of the print form whose property of the printed image is three kinds is shown.

[0068] Moreover, while using and printing the recording ink of an example and the

example of a comparison on the PET film which has the layer which uses PVA as a principal component on a front face, it printed repeatedly using the Magenta color recording ink and yellow color recording ink which were prepared independently, the PET film which has the printing image was projected with the over head projector, and color-enhancing evaluation was performed. In Table 6, O mark has high transparency, and also in one color, although it is somber, as for x mark, color nonuniformity and the case where it is are shown for the case where, as for \*\* mark, coloring of blue and glee is a little somber in the case where coloring of blue and glee is good although \*\* of monochromatic coloring is good.

[0069] 2) The waterproof printing image sample of an image was immersed in 30-degree C water for 1 minute, change of the image concentration before and behind processing was measured with the Macbeth concentration meter, and it asked for the water resisting property (rate of fading %) by the following formula. In Table 6, the case where x mark is 30% or more when \*\* mark is less than 30% 20% or more about the case where the water resisting property (rate of fading %) of O mark is less than 20% also in any of three kinds of print forms is shown.

Rate (%) of fading =  $[1 - (\text{image concentration before} / \text{image concentration after processing})] \times 100$  [0070] 3) Time amount until it pushes a filter paper against the image after drying printing of an image on fixed conditions and recording ink stops imprinting in a filter paper was measured. In Table 6, the case where it dried within in 10 seconds also in any of three kinds of print forms was considered as O mark, and the case where the time amount beyond it was required was shown as a x mark.

[0071] 4) Preservation stability each recording ink was put into the polyethylene container, it saved for three months under each conditions (-20 degrees C, 5 degrees C, 20 degrees C, and 70 degrees C), and the surface tension after preservation, viscosity, and the existence of a settlements deposit were investigated. In Table 6, even if saved on which conditions, although there were not O mark and precipitate about the case where there is no change of physical properties etc., the case where the deposit of \*\* mark and precipitate was accepted in the case where physical-properties change is large was shown as a x mark.

[0072] 5) When the ink jet printer equipped with 30 micrometers of diameters of a printing relaxation time dependability nozzle and the head driven by PZT which has the nozzle of 128 was used, a printing pause was carried out without performing cap, cleaning, etc. working, and which carried out a time amount printing pause, whether the injection direction shifts by the carriage return or the weight of a discharged liquid drop changes estimated the dependability. In Table 6, change of drop weight was small at O mark and the printing pause for 600 seconds in the case where it is satisfactory at especially the printing pause for 600 seconds, and the case where remarkable blinding generated the case where a gap of the injection direction is small, in \*\* mark and the printing pause for less than 600 seconds was shown as a x mark.

[0073]

[Table 6]

	画像の 鮮明性	画像の 耐水性	画像の 乾燥性	記録液 保存性	吐出信頼性	OHP 適性
実施例 1	○	○	○	○	○	○
実施例 2	○	○	○	○	○	○
実施例 3	○	○	○	○	○	○
実施例 4	○	○	○	○	○	○
実施例 5	○	○	○	○	○	○
実施例 6	○	○	○	○	○	○
実施例 7	○	○	○	○	○	○
実施例 8	○	○	○	○	○	○
実施例 9	○	○	○	○	○	○
実施例 10	○	○	○	○	○	○
比較例 1	△(色調)	×	○	○	○	○
比較例 2	△(色調)	△	○	△(経路)	△	○
比較例 3	×	○	×	×(経路)	×	△
比較例 4	×	○	×	×	△	△
比較例 5	○	×	○	○	○	△
比較例 6	×	○	×	×	×	×
比較例 7	△	△	○	×	△	×

[0074] When the recording ink obtained according to the example is used so that clearly from Table 6, it excels in the color reproduction nature of a color picture, and there is no image blot, it is a clear image with high concentration, and the image excellent in the water resisting property can be obtained also when which print form is used, and it excels also in drying [ of an image ]. Furthermore, the recording ink obtained according to the example is excellent in preservation stability, and can perform ink jet record with high regurgitation dependability after a printing pause after prolonged preservation.

[0075] On the other hand, color tone change of an image was large, and the recording ink of the water resisting property of an image obtained by the example 1 of a comparison was inadequate, in the recording ink obtained by the example 2 of a comparison, color tone change of an image was large, and it was inferior to the water resisting property of an image, and physical-properties change of recording ink was large in low temperature. It was that in which the concentration unevenness by the lack of drying occurs, and is inferior to the clear nature of an image in the recording ink obtained by the examples 3, 4, and 6 of a comparison, and the distributed stability of a coloring agent is inferior to the preservation stability and regurgitation dependability of recording ink bad. Moreover, the preservation stability of recording ink was bad insufficiently [ the recording ink of the water resisting property of an image obtained by the example 5 of a comparison is inadequate, and / the recording ink obtained by the example 7 of a comparison / the clear nature of an image, or the water resisting property of an image ]. Furthermore, when the recording ink obtained according to the example was used, OHP fitness was good, but when the recording ink obtained by the examples 3-7 of a comparison was used, it was a thing inferior to OHP fitness.

[0076]

[Effect of the Invention] According to this invention, the recording ink which has a color tone good as a cyanogen color, and was excellent in the color reproduction nature of a color picture, and was excellent in the water resisting property of a record

image and lightfastness can be obtained. The recording ink which can form the image which was excellent in blue and the color reproduction nature of Green, and excelled [ sheet / for over head projectors / transparence ] in transparency especially can be obtained. According to this invention, it excels in drying [ of the record image formed in the regular paper ], and a blot of an image is prevented, and the recording ink which can form a clear image can be obtained. According to this invention, it excels in preservation stability and recording ink with the high regurgitation dependability in ink jet record can be obtained also in after prolonged preservation. Moreover, according to this invention, recording ink excellent in the regurgitation dependability after the printing pause in ink jet record can be obtained. Furthermore, by the ink jet record approach using the recording ink of this invention, it excels in a water resisting property and lightfastness, and color reproduction nature is good and can form the color picture excellent in clear nature with high resolution.

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最終頁に続く

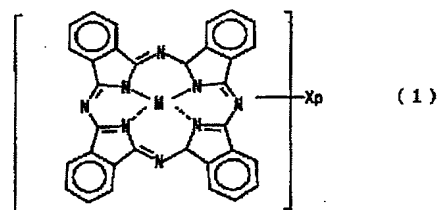
(54) 【発明の名称】 記録液及びそれを用いた記録方法

(57) 【要約】

【課題】 シアン色として良好な色調を有しカラー画像の色再現性に優れ、且つ記録画像の耐水性および耐光性が良好であり、また普通紙に形成された記録画像の乾燥性に優れ、且つ画像のにじみが防止され、鮮明な画像を形成することができる記録液、及びそれを用いた記録方法を提供する。

【解決手段】 水に分散または溶解する着色剤、水および湿潤剤を主成分とする記録液において、着色剤として一般式 (1) で表されるフタロシアン化合物の少なくとも 1 種と遊離酸型で示されるカルボン酸基が導入されたフタロシニン化合物の少なくとも 1 種とを同時に含有し、分散剤として親水性部分と疎水性部分をもった高分子化合物及び／または炭素数 5 以上のアルキル基を有する界面活性剤を含有する。

【化 1】





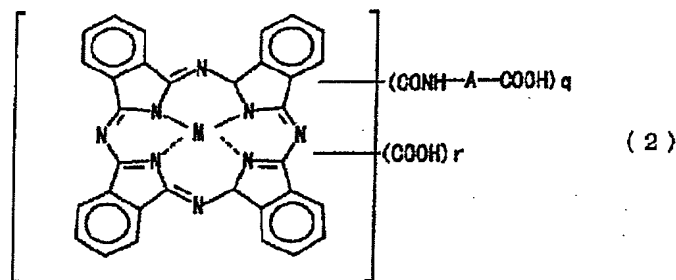
(2)

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## 【特許請求の範囲】

【請求項1】 水に分散または溶解する着色剤、水および湿潤剤を主成分とする記録液において、着色剤として下記一般式(1)で表されるフタロシアニン化合物およびハロゲン置換フタロシアニン化合物の少なくとも1種と下記一般式(2)または(3)で表される遊離酸型で示されるカルボン酸基が導入されたフタロシアニン化合物の少なくとも1種とを同時に含有し、分散剤として親水性部分と疎水性部分をもった高分子化合物及び／または炭素数5以上のアルキル基を有する界面活性剤を含有することを特徴とする記録液。

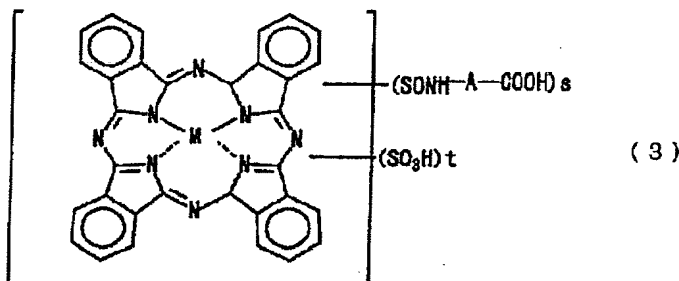
## 【化1】



(式中、Mは水素原子、Cu、Fe、Co、Niを表し、Aはフェニレン基、分岐していてもよい炭素数1以上のアルキレン基を表す。qは0から4の整数、rは0\*

\*から8の整数を表し、qとrは同時に0になることはない。)

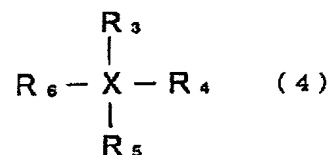
## 【化3】



(式中、Mは水素原子、Cu、Fe、Co、Niを表し、Aはフェニレン基、分岐していてもよい炭素数1以上のアルキレン基を表す。sは0から4の整数、tは0から4の整数を表し、sとtは同時に0になることはない。)

【請求項2】 一般式(1)で表されるフタロシアニン化合物の記録液中における粒子径が0.01μm乃至0.1μmであり、一般式(2)または(3)で表されるフタロシアニン化合物の対イオンがナトリウム、リチウム、あるいは下記一般式(4)で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンイオンであることを特徴とする請求項1記載の記録液。

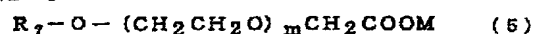
## 【化4】



(式中、Xは窒素原子またはリン原子を表し、R<sub>3</sub>、R<sub>4</sub>、R<sub>5</sub>およびR<sub>6</sub>は水素原子、炭素数1乃至4のアルキル基、ヒドロキシルアルキル基、ハロゲン化アルキル基を表す。)

【請求項3】 界面活性剤として下記一般式(5)で表されるポリオキシエチレンアルキルエーテル酢酸塩及び／または下記一般式(6)で表されるジアルキルスルホ琥珀酸塩を含有し、表面張力が50mN/m以下であることを特徴とする請求項1または2記載の記録液。

## 【化5】



(式中、R<sub>7</sub>は炭素数6乃至14の分岐していてもよい

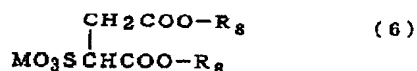
10 (式中、Mは水素原子、Cu、Fe、Co、Niを表す。Xはハロゲン原子を表し、pは0から8の整数を表す。)

## 【化2】

(3)

アルキル基を表し、Mはアルカリ金属イオン、第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンを表す。mは3から12の整数を表す。)

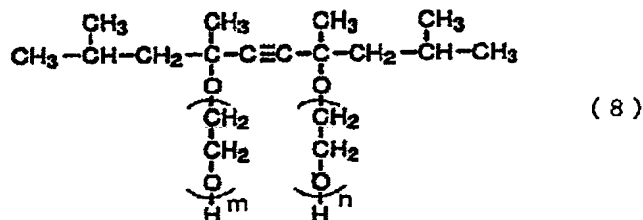
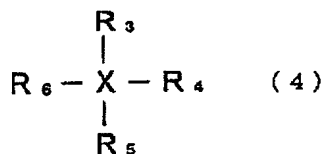
【化6】



(式中、R<sub>8</sub>は炭素数5乃至7の分岐したアルキル基を表し、Mはアルカリ金属イオン、第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンを表す。)

【請求項4】 一般式(5)または(6)で表される化合物の対イオンがナトリウム、リチウム、あるいは下記一般式(4)で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンイオンであることを特徴とする請求項3記載の記録液。

【化4】



(式中、m、nは0から20の整数を表す。)

【請求項6】 さらに尿素及び尿素誘導体を含有することを特徴とする請求項5記載の記録液。

【請求項7】 湿潤剤としてピロリドン誘導体の少なくとも1種を含有することを特徴とする請求項1、2、3、4、5または6何れか記載の記録液。

【請求項8】 pHが6以上11以下であることを特徴とする請求項1、2、3、4、5、6または7何れか記載の記録液。

【請求項9】 請求項1乃至8の記録液を熱エネルギーまたは機械エネルギーにより微小な液滴として飛翔させ、ステキヒトサイズ度が3秒以上の記録用紙に記録液を20 p l/mm<sup>2</sup>乃至200 p l/mm<sup>2</sup>付着せしめることにより、解像度10ドット/mm×10ドット/mm以上の画像を形成することを特徴とする記録方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、インクジェット記録、水性筆記用具、記録計あるいはペンプロッターなどに用いるのに適した記録液に関し、特にインクジェット記録用に適した記録液、更には所謂普通紙に対するカラ

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(式中、Xは窒素原子またはリン原子を表し、R<sub>3</sub>、R<sub>4</sub>、R<sub>5</sub>およびR<sub>6</sub>は水素原子、炭素数1乃至4のアルキル基、ヒドロキシアルキル基、ハロゲン化アルキル基を表す。)

【請求項5】 下記一般式(7)または化学式(8)で表される界面活性剤を含有し、表面張力が50 mN/m以下であることを特徴とする請求項1、2または3記載の記録液。

【化7】



(式中、Rは分岐していてもよい炭素数6乃至14の炭素鎖を表し、kは5から12の整数を表す。)

【化8】

一画像形成用として特に優れた特性を示すインクジェット記録用の記録液に関するものである。たま、本発明はその記録液を用いた記録方法に関するものである。

【0002】

【従来の技術】近年、インクジェットプリンターは低騒音、低ランニングコストといった利点から普及し、普通紙に印字可能なカラープリンターも市場に投入されている。この様なインクジェットプリンターにおいては、カラー画像の色再現性、画像の耐水性および耐光性、画像の乾燥性、画像にじみ防止、および吐出信頼性を満足させることが必要であり、普通紙上におけるカラー画像の色再現性と耐光性および耐水性とを両立させるために、インクジェットプリンター用記録液に用いる染料や顔料の改良が行われているが、記録画像の耐光性や耐水性を向上させ且つ吐出信頼性を高め、しかも色再現性に優れた記録液を得ることは困難であった。例えば、シアンの記録液としては、カルボン酸基を導入した銅フタロシアニン系染料を用いた記録液が特開昭63-210175号公報、特開平1-126381号公報あるいは特開平1-19077号公報などに開示されているが、耐水性はスルホン酸基を導入したフタロシアニン系染料

(4)

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に比べて向上するものの耐光性が不十分であり光によって褪色するため、長期間日光にさらされるポスター等に使用することが困難である。また、記録画像の耐水性および耐光性を得るために顔料を用いることも種々試みられているが、色調に問題があるため、現状では特に耐光性の要求される大型のプロッター以外では採用されていない。また、顔料を用いた場合には、記録画像の高解像度化に対応するインクジェットプリンターなどで目詰まりが発生し吐出信頼性に欠けるという問題もある。

【0003】そこで、色調を改良しカラー画像の色再現性を向上させ、また画像の耐光性、耐水性、および吐出信頼性を改良するために顔料と染料を混合して用いることが試みられ、例えば特公昭60-45668号公報には、水溶性青色染料と青色顔料、および高分子分散剤と水から主としてなる記録液が開示されているが、染料の耐光性や耐水性が不十分であり、また普通紙への記録液の浸透性や発色性が必ずしも十分でなかった。

【0004】一方、カラー画像の形成、特にインクジェットプリンターによってカラー画像を形成する場合、イエロー、マゼンタ、シアンの単色印字部で鮮明な画像が形成されても、レッド、グリーン、ブルーの2色重ね部分およびその色境界でにじみが発生しやすく画像の鮮明性が低下するという欠点がある。

【0005】特に定着装置を用いないでインクジェット記録による記録画像の乾燥を行う場合、特開昭55-29546号公報などのように記録紙に対する記録液の浸透性を高めることによって記録画像の乾燥性を向上させているため、使用する記録紙により画像のにじみが著しくなり画像の鮮明性が低下するという欠点がある。

【0006】特公昭60-23793号公報には記録液に界面活性剤としてジアルキルスルホコハク酸塩を含有させることにより、インクジェット記録による記録画像の乾燥性を向上させると共に画像の鮮明性の低下を少なくすることが開示されているが、使用する記録紙により、画素径が著しく異なり画像濃度の低下も著しく画像の鮮明性が低下するといった不具合があり、また記録液がアルカリ側では界面活性剤が分解し、記録液の保存中に界面活性剤の効果がなくなり記録紙に対する濡れ性が低下するため、画像の乾燥性が変化し色境界での画像劣化が発生するという欠点がある。

【0007】さらに、特開昭56-57862号公報等には、記録液に強塩基性物質を含有させることにより、インクジェット記録による記録画像の乾燥性を向上させることが開示されているが、ロジンサイズされた酸性紙に画像を形成した場合には乾燥性を向上させる効果があるもののアルキルケテンダイマーやアルケニルスルホコハク酸をサイズ剤として用いた記録紙では乾燥性向上の効果がみられず、また、酸性紙でも記録画像における2色重ね部分では乾燥性向上の効果がみられないという欠点がある。また、特開平1-203483号公報には記

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録液に多価アルコール誘導体及びペクチンを含有させ、増粘剤としてのペクチンにより記録画像のにじみを防止することが開示されているが、ペクチンは水酸基を親水基とする非イオン性化合物であるため、印字休止後の吐出信頼性に欠けるという欠点がある。

【0008】

【発明が解決しようとする課題】従来においては、良好な色調を有しカラー画像の色再現性に優れ、記録画像の耐水性および耐光性が十分であり、更にインクジェット記録における吐出信頼性の高い記録液を得ることが困難であった。また、さらに普通紙に形成された記録画像の乾燥性に優れ、且つ画像のにじみが防止され、鮮明な画像を形成することのできる記録液を得ることが困難であった。そこで本発明の第1の課題はこのような問題点を解決し、特にシアン色として良好な色調を有しカラー画像の色再現性に優れ、且つ記録画像の耐水性および耐光性に優れた記録液を提供することにある。特に、ブルーとグリーンの色再現性に優れ、オーバーヘッドプロジェクター用透明シートに透明性の優れた画像を形成することのできる記録液を提供することにある。本発明の第2の課題は、普通紙に形成された記録画像の乾燥性に優れ、且つ画像のにじみが防止され、鮮明な画像を形成することのできる記録液を提供することにある。本発明の第3の課題は、保存安定性に優れ、長期間の保存後においても、インクジェット記録における吐出信頼性の高い記録液を提供することにある。また、本発明の第4の課題は、インクジェット記録における印字休止後の吐出信頼性に優れた記録液を提供することにある。さらに、本発明の第5の課題は、耐水性および耐光性に優れ、色再現性が良好で鮮明性に優れたカラー画像を高解像度で形成することのできるインクジェット記録方法を提供することにある。

【0009】

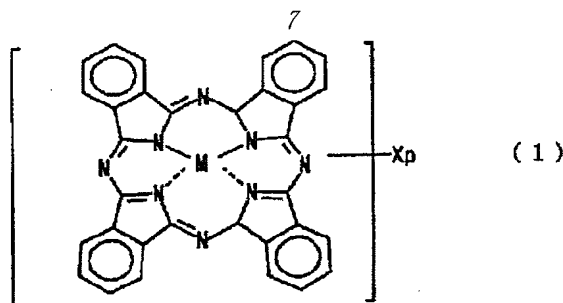
【課題を解決するための手段】本発明の上記課題は、水に分散または溶解する着色剤、水および湿潤剤を主成分とする記録液において、着色剤として下記一般式(1)で表されるフタロシアニン化合物およびハロゲン置換フタロシアニン化合物の少なくとも1種と下記一般式

(2)または(3)で表される遊離酸型で示されるカルボン酸基が導入されたフタロシニン化合物の少なくとも1種とを同時に含有し、分散剤として親水性部分と疎水性部分をもった高分子化合物及び／または炭素数5以上のアルキル基を有する界面活性剤を含有することを特徴とする記録液によって達成される。

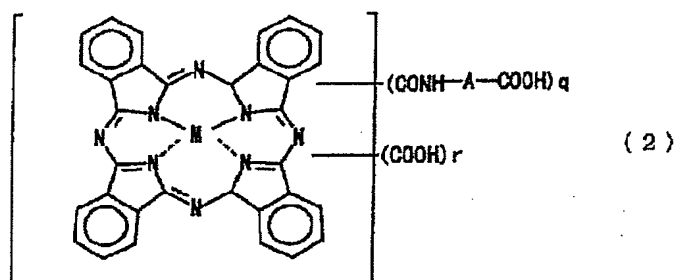
【化1】

50

(5)

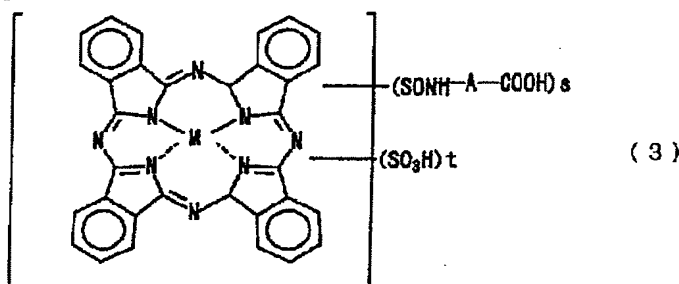


(式中、Mは水素原子、Cu、Fe、Co、Niを表す。Xはハロゲン原子を表し、pは0から8の整数を表す。)  
【化2】



(式中、Mは水素原子、Cu、Fe、Co、Niを表し、Aはフェニレン基、分岐していてもよい炭素数1以上のアルキレン基を表す。qは0から4の整数、rは0 \* 20

\*から8の整数を表し、qとrは同時に0になることはない。)  
【化3】



(式中、Mは水素原子、Cu、Fe、Co、Niを表し、Aはフェニレン基、分岐していてもよい炭素数1以上のアルキレン基を表す。sは0から4の整数、tは0から4の整数を表し、sとtは同時に0になることはない。)

【0010】一般式(1)で表されるフタロシアニン化合物の少なくとも1種と、一般式(2)または(3)で表される遊離酸型で示されるカルボン酸基が導入されたフタロシアニン化合物の少なくとも1種とを着色剤として同時に用いることにより、シアン色として良好な色調を有しカラー画像の色再現性に優れ、且つ記録画像の耐水性および耐光性に優れた記録液を得ることができる。特に、この記録液によればブルーとグリーンの色再現性に優れた画像を形成することができ、またオーバーヘッドプロジェクター用透明シートに透明性の優れた画像を形成することができる。

【0011】これは、一般式(1)で表されるフタロシアニン化合物を着色剤として用いた場合、それを微粒子化しても単独では色相や彩度が不十分でありカラー画像

の色再現性に劣っているが、一般式(2)または(3)で表される遊離酸型で示されるカルボン酸基が導入されたフタロシアニン化合物の少なくとも1種と共に用いることにより、色相の調整や彩度の向上を図ることができ、且つこれらのフタロシアニン化合物が耐水性および耐光性に優れていることによるものである。また、分散剤として親水性部分と疎水性部分をもった高分子化合物及び/または炭素数5以上のアルキル基を有する界面活性剤を含有させることにより、記録液の普通紙などの記録紙に対する浸透性を高めて記録画像の乾燥性を向上させ、且つ画像の滲みを防止して鮮明な画像を形成することができる。

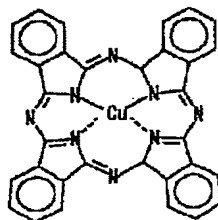
【0012】本発明における一般式(1)、(2)または(3)で表されるフタロシアニン化合物の具体例としては、それぞれ表1、表2または表3に示ものを挙げることができる。

【0013】

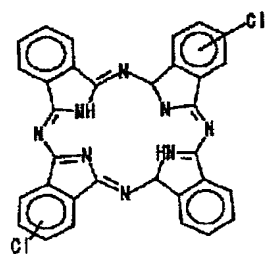
【表1】

(6)

<sup>9</sup>  
(1-1)

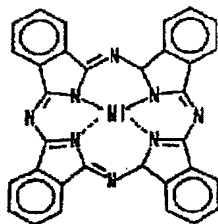


(1-5)

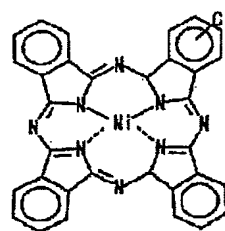


10

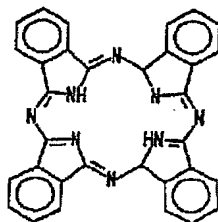
(1-2)



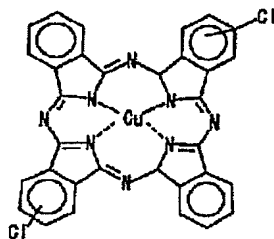
(1-6)



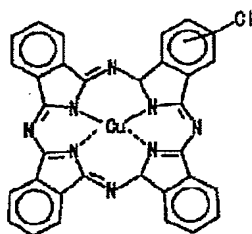
(1-3)



(1-7)



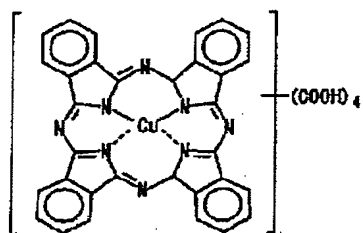
(1-4)



【0014】

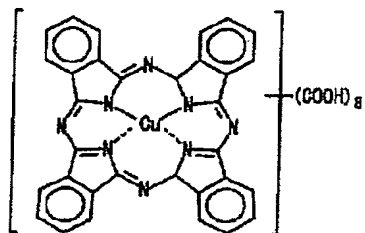
【表2】

(7)

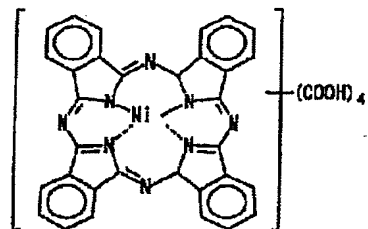
11  
(2-1)

(2-2)

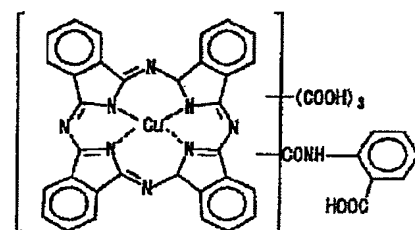
12



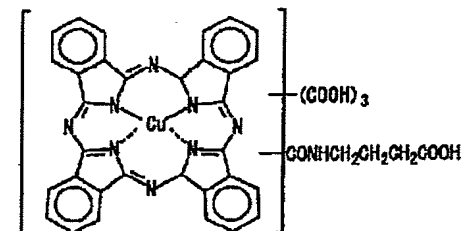
(2-3)



(2-4)



(2-5)



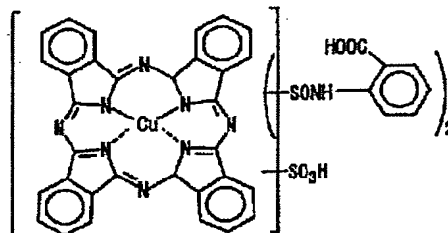
【0015】

【表3】

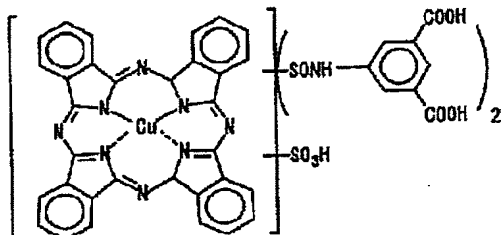
(8)

13

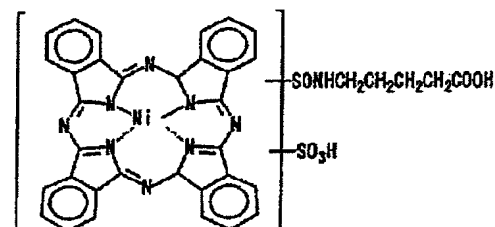
(3-1)



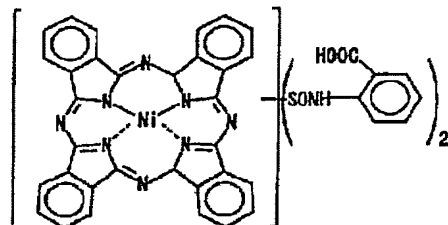
(3-2)



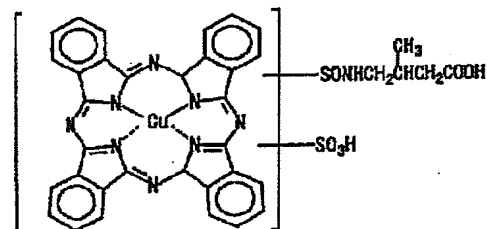
(3-3)



(3-4)



(3-5)



【0016】なお、これらのフタロシアニン化合物は合成段階での不純物として多価金属イオンや塩化物イオン、硫酸イオンなどを含有している場合があり、イオン交換樹脂や逆浸透膜、限外濾過などにより精製して用いることが好ましい。精製して用いることにより、インク

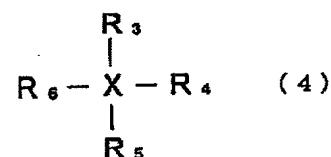
ジェットプリンターにおいてノズルの目詰まりを防止することができる。

【0017】一般式(1)で表されるフタロシアニン化合物は、微粒子化して用いられ、その記録液中における粒子径としては0.01~0.1μmが好ましい。また、一般式(2)または(3)で表されるフタロシアニン化合物の対イオンをナトリウム、リチウム、あるいは下記一般式(4)で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンイオンとする

ことにより、一般式(2)または(3)で表されるフタロシアニン化合物の溶解安定性を向上させることができる。

【0018】

【化4】



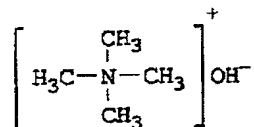
(式中、Xは窒素原子またはリン原子を表し、R<sub>3</sub>、R<sub>4</sub>、R<sub>5</sub>およびR<sub>6</sub>は水素原子、炭素数1乃至4のアルキル基、ヒドロキシアルキル基、ハロゲン化アルキル基を表す。)

(9)

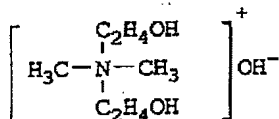
15

一般式(2)または(3)で表されるフタロシアニン化合物の対イオンをこのようにするには、例えば、水酸化ナトリウム、水酸化リチウムあるいは下記表4に示す水\*

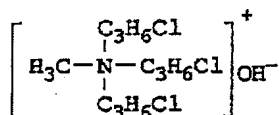
(4-1)



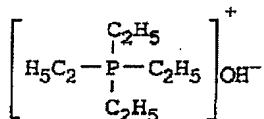
(4-3)



(4-5)



(4-7)



(4-9)



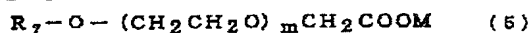
【0020】上記のように、一般式(1)で表されるフタロシアニン化合物微粒子の記録液中における粒子径を0.01~0.1μmとし、また一般式(2)または

(3)で表されるフタロシアニン化合物の対イオンをナトリウム、リチウム、あるいは前記一般式(4)で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンイオンとすることにより、記録液の保存安定性を向上させることができ、記録液をインクジェットプリンター用として用いた場合に、ノズルの目詰まりを発生させることがなく、吐出信頼性の高い記録を行うことができる。

【0021】次に、本発明において用いられる分散剤について説明する。炭素数5以上のアルキル基を有する界面活性剤としては、アニオン系界面活性剤である下記一般式(5)で表されるポリオキシエチレンアルキルエーテル酢酸塩または下記一般式(6)で表されるジアルキルスルホ琥珀酸塩が好ましい。

【0022】

【化5】



(式中、R<sub>7</sub>は炭素数6乃至14の分岐していてもよいアルキル基を表し、Mはアルカリ金属イオン、第4級ア

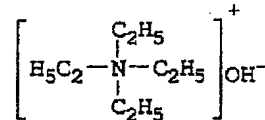
16

\* 酸化物等を記録液に添加すればよい。

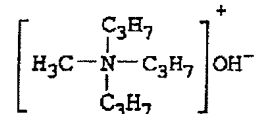
【0019】

【表4】

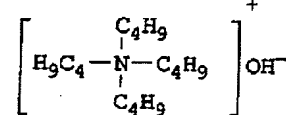
(4-2)



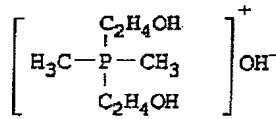
(4-4)



(4-6)



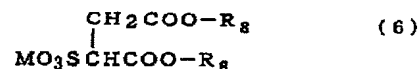
(4-8)



ンモニウム、第4級ホスホニウムまたはアルカノールアミンを表す。mは3から12の整数を表す。)

【0023】

【化6】



(式中、R<sub>8</sub>は炭素数5乃至7の分岐したアルキル基を表し、Mはアルカリ金属イオン、第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンを表す。)

【0024】これらのアニオン系界面活性剤を用いることにより、普通紙などの記録紙に対する記録液の浸透性を高め記録画像の乾燥性を向上させ、且つ画像のにじみを防止して鮮明性に優れた画像を形成することができる。特に、これらの界面活性剤を用い、記録液の表面張力を50mN/m以下、より好ましくは40mN/m以下とすることにより、記録液と普通紙などの記録紙表面との濡れ性をより向上させることができ、記録紙に対する記録液の浸透性を高めて記録画像の乾燥性を向上させ、且つ画像のにじみを防止して鮮明性に優れた画像を形成することができる。

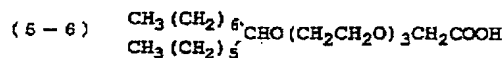
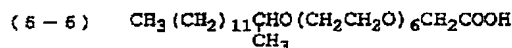
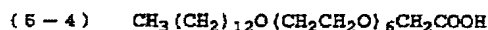
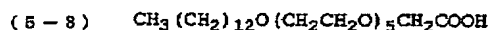
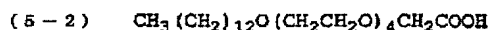
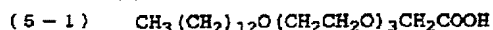


(10)

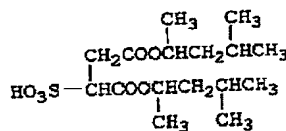
17

【0025】本発明における表面張力は記録液の記録紙への浸透性を示す指標であり、特に表面形成されて1秒以下の短い時間での動的表面張力を示し、飽和時間で測定される静的表面張力とは異なるものである。測定法としては特開昭63-31237号公報等に記載されている従来公知の方法で1秒以下の動的な表面張力を測定できる方法であればいずれも使用できるが、ここではWilhelmy式の吊り板式表面張力計を用いて測定した値を示している。

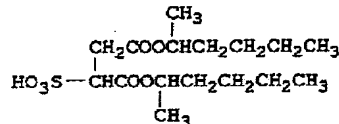
【0026】なお、上記のアニオン系界面活性剤を用い\*10 【表5】



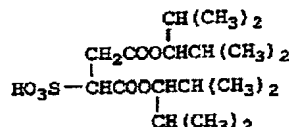
(6-1)



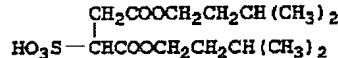
(6-2)



(6-3)



(6-4)



【0029】一般式(5)で表されるポリオキシエチレンアルキルエーテル酢酸塩または一般式(6)で表されるジアルキルスルホ琥珀酸塩の対イオンMとしては、ナトリウム、リチウム、あるいは前記一般式(4)で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンイオンが特に好ましい。対イオンMをこのようにすることにより、これらアニオン系界面活性剤の溶解安定性をより向上させ、保存安定性により優れた記録液を得ることができる。それにより記録液を長期間保存した後においても、インクジェット記録において吐出信頼性の高い記録をおこなうことができる。対イオンMをこのようにするには、例えば、水酸化ナトリウム、水酸化リチウムあるいは前記表4に示す水酸化物などを記録液に添加すればよい。

【0030】一般式(5)で表されるポリオキシエチレンアルキルエーテル酢酸塩または一般式(6)で表されるジアルキルスルホ琥珀酸塩の記録液における含有量としては、0.05~10重量%が好ましい。この含有量

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\*ることにより、画像のにじみを防止して鮮明性に優れた画像を形成することができるのは、普通紙などの記録紙表面より供給されるプロトンにより記録液が増粘し、それにより、にじみが少なくなるためと推定される。

【0027】一般式(5)で表されるポリオキシエチレンアルキルエーテル酢酸塩または一般式(6)で表されるジアルキルスルホ琥珀酸塩の具体例を遊離酸型で下表5に示す。

【0028】

の範囲でインクジェット記録に要求される記録紙に対する浸透性を記録液に与えることができる。0.05重量%よりも少なくなると2色重ね部の境界でのにじみが発生し、10重量%を越えると一般式(5)または(6)で表されるアニオン系界面活性剤自体が低温で析出し易くなり、また一般式(2)または(3)で表されるフタロシニン化合物が析出することがあり、インクジェット記録における吐出信頼性が低下するようになる。

【0031】なお、上記のように、本発明の記録液において一般式(2)または(3)で表されるフタロシニン化合物の対イオン、あるいは一般式(5)または

(6)で表されるアニオン系界面活性剤の対イオンMをナトリウム、リチウム、あるいは前記一般式(4)で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミン陽イオンとすることにより、それらフタロシニン化合物あるいはアニオン系界面活性剤の溶解安定性を向上させることができるが、対イオンがすべてがナトリウム、リチウムあるいは前記一般式(4)

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で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンイオンである必要はなく、他のアルカリイオンとの混合とすることもできる。ナトリウム、リチウムあるいは前記一般式(4)で表される第4級アンモニウム、第4級ホスホニウムまたはアルカノールアミンイオンの量としては、一般式(2)または

(3)で表されるフタロシニン化合物およびアニオン系界面活性剤のモル数に対して30%以上が好ましく、特に50%以上が好ましい。

【0032】また、炭素数5以上のアルキル基を有する界面活性剤として、非イオン系界面活性剤である下記一般式(7)で表されるポリオキシエチレンアルキルフェニルエーテルまたは下記一般式(8)で表されるアセチレングリコール系界面活性剤も好ましいものである。

【0033】

【化7】

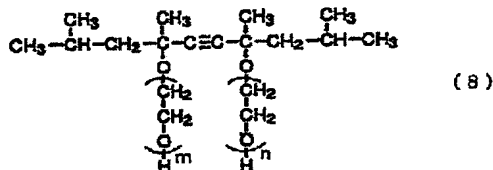


(式中、Rは分岐していてもよい炭素数6乃至14の炭素鎖を表し、kは5から12の整数を表す。)

炭素鎖としては、アルキル基、アルケニル基などが挙げられる。

【0034】

【化8】



(式中、m、nは0から20の整数を表す。)

【0035】これらの非イオン系界面活性剤を用いることにより、普通紙などの記録紙に対する記録液の浸透性を高め記録画像の乾燥性を向上させ、且つ画像の滲みを防止して鮮明性に優れた画像を形成することができる。特に、これらの非イオン系界面活性剤を用い、記録液の表面張力を50mN/m以下とすることにより、記録液と普通紙などの記録紙表面との濡れ性をより向上させることができ、記録紙に対する記録液の浸透性を高めて記録画像の乾燥性を向上させ、且つ画像の滲みを防止して鮮明性に優れた画像を形成することができる。更に、これら非イオン系界面活性剤と共に尿素、あるいはヒドロキシエチル尿素またはジヒドロキシエチル尿素などの尿素誘導体を用いることにより、前記一般式(1)、

(2)または(3)で表されるフタロシニン化合物と非イオン系界面活性剤との間の相互作用を弱めフタロシニン化合物の会合を緩和することで浸透性を向上させ、またインクジェット記録における吐出信頼性や記録液の長期保存性を改良することができる。これら尿素や尿素誘導体の添加量としては、0.1~5重量%が好ましい。

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0.1重量%よりも少ないと効果がなく、また5重量%を越えると水分蒸発時の粘度変化に影響をおよぼし吐出信頼性を損なうことがある。

【0036】さらに、顔料分散剤として、親水性部分と疎水性部分を有する高分子化合物を用いることが好ましく、このような親水性部分と疎水性部分を有する高分子化合物としては、親水性高分子として、例えば天然系ではアラビアガム、トラガンガム、グーアガム、カラヤガム、ローカストビーンガム、アラビノガラクトン、ペクチン、クインシードデンプン等の植物性高分子、アルギン酸、カラギーナン、寒天等の海藻系高分子、ゼラチン、カゼイン、アルブミン、コラーゲン等の動物系高分子、キサンテンガム、デキストラン等の微生物系高分子、などが挙げられ、半合成系ではメチルセルロース、エチルセルロース、ヒドロキシエチルセルロース、ヒドロキシプロピルセルロース、カルボキシメチルセルロース等の繊維素系高分子、デンプングリコール酸ナトリウム、デンプンリン酸エステルナトリウム等のデンプン系高分子、アルギン酸ナトリウム、アルギン酸プロピレングリコールエステル等の海藻系高分子などが挙げられる。また、純合成系ではポリビニルアルコール、ポリビニルピロリドン、ポリビニルメチルエーテル等のビニル系高分子、非架橋ポリアクリルアミド、ポリアクリル酸及びそのアルカリ金属塩、水溶性スチレンアクリル樹脂等のアクリル系樹脂、水溶性スチレンマレイン酸樹脂、水溶性ビニルナフタレンアクリル樹脂、水溶性ビニルナフタレンマレイン酸樹脂、8-ナフタレンスルホン酸ホルマリン縮合物のアルカリ金属塩、四級アンモニウムやアミノ基等のカチオン性官能基の塩を側鎖に有する高分子化合物などが挙げられる。またセラック等の天然高分子化合物も用いることができる。

【0037】本発明の記録液は上記の諸成分が水に分散または溶解されているものであるが、さらに記録液の保管時における乾燥を防止するため、あるいは一般式

(2)または(3)で表されるフタロシニン化合物の溶解安定性を向上させるため等の目的で、本発明の記録液には湿潤剤として水溶性有機溶媒が添加されている。

【0038】このような水溶性有機溶媒としては、例えば、エチレングリコール、ジエチレングリコール、トリエチレングリコール、ポリエチレングリコール、ポリプロピレングリコール、1,5ペンタンジオール、1,6ヘキサンジオール、グリセロール、1,2,6-ヘキサントリオール、1,2,4-ブタントリオール、1,2,3-ブタントリオール、ペトリオール等の多価アルコール類、エチレングリコールモノエチルエーテル、エチレングリコールモノブチルエーテル、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノエチルエーテル、ジエチレングリコールモノブチルエーテル、テトラエチレングリコールモノメチルエーテル、プロピレングリコールモノエチルエーテル等の多価アル

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コールアルキルエーテル類、エチレングリコールモノフェニルエーテル、エチレングリコールモノベンジルエーテル等の多価アルコールアリアルエーテル類、N-メチル-2-ピロリドン、N-ヒドロキシエチル-2-ピロリドン、2-ピロリドン、1, 3-ジメチルイミダゾリジノン、ε-カプロラクタム等の含窒素複素環化合物、ホルムアミド、N-メチルホルムアミド、N, N-ジメチルホルムアミド等のアミド類、モノエタノールアミン、ジエタノールアミン、トリエタノールアミン、モノエチルアミン、ジエチルアミン、トリエチルアミン等のアミン類、ジメチルスルホキシド、スルホラン、チオジエタノール等の含硫黄化合物類、プロピレンカーボネート、炭酸エチレン、γ-ブチロラクトン等が例示でき、これらの水溶性有機溶媒は単独もしくは、複数混合して用いることができる。

【0039】これらの中で特に好ましい水溶性有機溶媒はジエチレングリコール、チオジエタノール、ポリエチレングリコール200~600、トリエチレングリコール、グリセロール、1, 2, 6-ヘキサントリオール、1, 2, 4-ブタントリオール、ペトリオール、1, 5-ペンタンジオール、N-メチル-2-ピロリドン、N-ヒドロキシエチル-2-ピロリドン、2-ピロリドン、1, 3-ジメチルイミダゾリジノンなどであり、これらの水溶性有機溶媒を用いることにより一般式(2)または(3)で表されるフタロシニン化合物の溶解安定性を向上させると共に水分蒸発を抑制して記録液の乾燥を防ぐことができ、記録液を長期間保存した後においても、また長期間印字を休止した場合においても、吐出信頼性に優れたインクジェット記録を行うことができる。また、特に、N-ヒドロキシエチル-2-ピロリドン等のピロリドン誘導体を記録液に添加した場合には、前記一般式(1)で表されるフタロシニン化合物微粒子の分散安定性を向上させることができ、記録液の保存安定性を更に向上させることができる。それにより記録液を長期間保存した後においても、インクジェット記録において更に吐出信頼性の高いインクジェット記録をおこなうことができる。

【0040】また、本発明の記録液には、表面張力を調整する目的で前記一般式(5)、(6)、(7)または(8)で表される界面活性剤以外に、ジエチレングリコールモノフェニルエーテル、エチレングリコールモノフェニルエーテル、エチレングリコールモノアリアルエーテル、ジエチレングリコールモノフェニルエーテル、ジエチレングリコールモノブチルエーテル、プロピレングリコールモノブチルエーテル、テトラエチレングリコールクロロフェニルエーテル等の多価アルコールのアルキルまたはアリアルエーテル類、ポリオキシエチレンポリオキシプロピレンブロック共重合体、フッ素系界面活性剤、あるいはエタノール、2-プロパノール等の低級アルコール類などを添加することができ、特にジエチレン

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グリコールモノブチルエーテルが好ましい。

【0041】本発明の着色材としては、前記一般式

(1)で表されるフタロシニン化合物の少なくとも1種と前記一般式(2)または(3)で表されるフタロシニン化合物の少なくとも1種とを同時に用いるほかに、必要に応じて、他の着色剤を混合して用いることができる。このような着色剤としては、カラーインデックスにおいて酸性染料、直接性染料、塩基性染料、反応性染料、食用染料に分類される水溶性染料で耐水性および耐光性が優れたもの、あるいは顔料などが用いられる。これらは耐水性や耐光性が疎外されない範囲で添加することが好ましい。

【0042】これらの染料を具体的に挙げれば、酸性染料及び食用染料としては、C. I. アシッドイエロー17, 23, 42, 44, 79, 142, C. I. アシッドレッド1, 8, 13, 14, 18, 26, 27, 35, 37, 42, 52, 82, 87, 89, 92, 97, 106, 111, 114, 115, 134, 186, 249, 254, 289, C. I. アシッドブルー9, 29, 45, 92, 249, C. I. アシッドブラック1, 2, 7, 24, 26, 94, C. I. フードイエロー3, 4, C. I. フードレッド7, 9, 14, C. I. フードブラック1, 2, 直接性染料としては、C. I. ダイレクトイエロー1, 12, 24, 26, 33, 44, 50, 86, 120, 132, 142, 144, C. I. ダイレクトレッド1, 4, 9, 13, 17, 20, 28, 31, 39, 80, 81, 83, 89, 225, 227, C. I. ダイレクトオレンジ26, 29, 62, 102, C. I. ダイレクトブルー1, 2, 6, 15, 22, 25, 71, 76, 79, 86, 87, 90, 98, 163, 165, 199, 202, C. I. ダイレクトブラック19, 22, 32, 38, 51, 56, 71, 74, 75, 77, 154, 168, 171, 塩基性染料としては、C. I. ベーシックイエロー1, 2, 11, 13, 14, 15, 19, 21, 23, 24, 25, 28, 29, 32, 36, 40, 41, 45, 49, 51, 53, 63, 64, 65, 67, 70, 73, 77, 87, 91, C. I. ベーシックレッド2, 12, 13, 14, 15, 18, 22, 23, 24, 27, 29, 35, 36, 38, 39, 46, 49, 51, 52, 54, 59, 68, 69, 70, 73, 78, 82, 102, 104, 109, 112, C. I. ベーシックブルー1, 3, 5, 7, 9, 21, 22, 26, 35, 41, 45, 47, 54, 62, 65, 66, 67, 69, 75, 77, 78, 89, 92, 93, 105, 117, 120, 122, 124, 129, 137, 141, 147, 155, C. I. ベーシックブラック2, 8, 反応性染料としては、C. I. リアクティブブラック3, 4, 7, 11, 12, 17, C. I. リアクティブイエロー1,

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5, 11, 13, 14, 20, 21, 22, 25, 40, 47, 51, 55, 65, 67, C. I. リアクティブレッド1, 14, 17, 25, 26, 32, 37, 44, 46, 55, 60, 66, 74, 79, 96, 97, C. I. リアクティブブルー1, 2, 7, 14, 15, 23, 32, 35, 38, 41, 63, 80, 95等が使用でき、特に酸性染料及び直接性染料が好ましい。

【0043】また、顔料としては、有機顔料としてアゾ系、フタロシアニン系、アントラキノン系、ジオキサジン系、インジゴ系、チオインジゴ系、ペリレン系、イソインドレノン系、アニリンブラック、アゾメチン系、ローダミンBレーキ顔料、カーボンブラック等が挙げられ、無機顔料として酸化鉄、酸化チタン、炭酸カルシウム、硫酸バリウム、水酸化アルミニウム、バリウムイエロー、紺青、カドミウムレッド、クロムイエロー、金属粉が挙げられる。

【0044】さらに、本発明の記録液には従来より知られている添加剤、例えば防腐防霉剤、防錆剤、pH調整剤、水溶性紫外線吸収剤または水溶性赤外線吸収剤などを添加することができる。

【0045】防腐防霉剤としてはデヒドロ酢酸ナトリウム、ソルビン酸ナトリウム、2-ピリジンチオール-1-オキシナトリウム、安息香酸ナトリウム、ペンタクロロフェノールナトリウムなどを用いることができ、防錆剤としては、酸性亜硫酸塩、チオ硫酸ナトリウム、チオジグリコール酸アンモン、ジイソプロピルアンモニウムニトライト、四硝酸ペンタエリスリトール、ジシクロヘキシルアンモニウムニトライトなどを用いることができる。

【0046】pH調整剤としては、調合される記録液に悪影響をおよぼさずにpHを6以上に調整できるものであれば、任意の物質を用いることができる。pH調整剤の具体例としては、ジエタノールアミン、トリエタノールアミン等のアミン、水酸化リチウム、水酸化ナトリウム、水酸化カリウム等のアルカリ金属元素の水酸化物、水酸化アンモニウム、第4級アンモニウム水酸化物、第4級ホスホニウム水酸化物、炭酸リチウム、炭酸ナトリウム、炭酸カリウム等のアルカリ金属の炭酸塩などが挙げられる。また、キレート試薬としては、例えば、エチレンジアミン四酢酸ナトリウム、ニトリロ三酢酸ナトリウム、ヒドロキシエチルエチレンジアミン三酢酸ナトリウム、ジエチレントリアミン五酢酸ナトリウム、ウラムニル二酢酸ナトリウムなどが使用できる。

\* 【0047】本発明の記録液におけるpHを6以上、特に6以上11以下に調整することにより、記録液の保存安定性が向上し、インクジェットプリンターなどにおける記録液カートリッジ内に長期間放置した場合でも、インクジェットノズルの目詰まりが生じることなくインクジェット記録を行うことができる。ただし、一般式(6)で表される界面活性剤を用いた場合には、pHが9以上では記録液の保存時に界面活性剤が分解し、記録液物性の変化が起こりやすいため一般式(6)で表される界面活性剤を用いる場合にはpHを6~9に調整することが好ましい。

【0048】本発明の記録液を用いてインクジェット記録を行うには、記録液を熱エネルギーまたは機械エネルギーにより、例えば20~60 $\mu$ m径の微細な吐出口より吐出させ、重量が10ng~160ngの液滴として速度5~20m/sで飛翔させてステキヒトサイズ度が3秒以上の記録用紙、特にステキヒトサイズ度が3秒以上の所謂普通紙に画像を形成することにより、耐水性および耐光性に優れ、色再現性が良好で鮮明性に優れたカラー画像を高解像度で形成することができる。特に、ステキヒトサイズ度が3秒以上の記録用紙に記録液を20pl/mm<sup>2</sup>乃至200pl/mm<sup>2</sup>付着せしめることにより、解像度10ドット/mm $\times$ 10ドット/mm以上の高解像度の画像を形成をすることができる。また、オフィスなどで一般に使用されているコピー用紙や用箋などはpHが5~6のものが多く、これらに本発明の記録液を用いてインクジェット記録を行うことにより、耐水性および耐光性に優れ、色再現性が良好で鮮明性に優れたカラー画像を高解像度で形成することができる。また、本発明の記録液を用いることにより、インクジェット記録用のオーバーヘッドプロジェクター(OHP)用透明シートに透明性の優れた画像を形成ことができ、OHP投影時に優れた発色を示すカラー画像を得ることができる。

【0049】

【実施例】以下に本発明を実施例により説明する。

【0050】実施例1

具体例(1-1)の化合物を分散剤の存在下で超音波ホモジェナイザーにて分散し粒子径を0.1 $\mu$ m以下とし、この分散液を用いて下記処方組成物を攪拌溶解し、pHが8.5になるように水酸化リチウム10%水溶液にて調整し、これを0.8 $\mu$ mのテフロンフィルターにて濾過し記録液1を得た。

具体例(1-1)の化合物	1.0重量%
具体例(2-1)の化合物	1.0重量%
スチレンアクリル酸重合体	0.4重量%
グリセロール	5重量%
N-ヒドロキシエチルピロリドン	5重量%
具体例(5-1)の界面活性剤	0.8重量%

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25	デヒドロ酢酸ナトリウム イオン交換水	26	0.2重量% 残量
【0051】実施例2	下記組成物を用い、pHを水酸化ナトリウムで8.8に*		*調整した以外は実施例1と同様にして記録液2を調製した。
	具体例(1-1)の化合物	1.2重量%	
	具体例(1-4)の化合物	0.8重量%	
	具体例(2-2)の化合物	0.6重量%	
	1,2,6-ヘキサントリオール	4重量%	
	1,5-ペンタンジオール	8重量%	
	具体例(5-1)の界面活性剤	1.2重量%	
	具体例(4-1)の25%水溶液	0.8重量%	
	アルギン酸ナトリウム	0.05重量%	
	尿素	5重量%	
	2-ピリジンチオール-1-オキシドナトリウム	0.2重量%	
	イオン交換水	残量	
【0052】実施例3	下記組成物を用い、pHを水酸化リチウムで8.5に調※		※整した以外は実施例1と同様にして記録液3を調製した。
	具体例(1-3)の化合物	1重量%	
	具体例(2-5)の化合物	0.5重量%	
	具体例(3-3)の化合物	0.5重量%	
	ジエチレングリコール	5重量%	
	グリセロール	5重量%	
	スチレンアクリル酸共重合体	0.5重量%	
	一般式(7)においてRがC <sub>9</sub> H <sub>19</sub> 、kが12の界面活性剤	2重量%	
	具体例(4-3)の25%水溶液	0.2重量%	
	デヒドロ酢酸ナトリウム	0.2重量%	
	イオン交換水	残量	
【0053】実施例4	下記組成物を用い、pHを水酸化リチウムで9.5に調★		★整した以外は実施例1と同様にして記録液4を調製した。
	具体例(1-3)の化合物	1.0重量%	
	具体例(3-1)の化合物	1.2重量%	
	エチレングリコール	5重量%	
	グリセロール	2重量%	
	1,5-ペンタンジオール	8重量%	
	2-ピロリドン	2重量%	
	ポリオキシエチレンポリオキシエチレンプロツク共重合体	1重量%	
	一般式(8)の界面活性剤(m、n=20)	0.8重量%	
	具体例(4-4)の25%水溶液	2重量%	
	尿素	5重量%	
	安息香酸ナトリウム	0.2重量%	
	イオン交換水	残量	
【0054】実施例5	下記組成物を用い、pHを水酸化ナトリウムで7.8に☆		☆調整した以外は実施例1と同様にして記録液5を調製した。
	具体例(1-4)の化合物	1.2重量%	
	具体例(2-1)の化合物	0.3重量%	
	具体例(3-3)の化合物	0.5重量%	
	トリエチレングリコール	5重量%	
	ペトリオール	10重量%	
	N-メチル-2-ピロリドン	5重量%	
	具体例(6-1)の界面活性剤	2重量%	

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具体例(4-2)の25%水溶液	1.5重量%
ヒドロキシエチル尿素	5重量%
2-ピリジンチオール-1-オキサイドナトリウム	0.2重量%
イオン交換水	残量

## 【0055】実施例6

\*た以外は実施例1と同様にして記録液6を調製した。

下記組成物を用い、pHを水酸化リチウムで8に調整し\*

具体例(1-3)の化合物	1.5重量%
具体例(2-5)の化合物	1.6重量%
2-ピロリドン	8重量%
グリセロール	7重量%
一般式(8)の界面活性剤(m+n=15)	1重量%
一般式(8)の界面活性剤(m, n=0)	1重量%
具体例(4-7)の25%水溶液	2重量%
ヒドロキシエチル尿素	5重量%
デヒドロ酢酸ナトリウム	0.2重量%
イオン交換水	残量

## 【0056】実施例7

※た以外は実施例1と同様にして記録液7を調製した。

下記組成物を用い、pHを水酸化リチウムで8に調整し※

具体例(1-1)の化合物	1.2重量%
具体例(1-5)の化合物	0.3重量%
具体例(3-2)の化合物	0.8重量%
N-メチル-2-ピロリドン	8重量%
1,5-ペンタンジオール	8重量%
具体例(5-4)の界面活性剤	0.8重量%
安息香酸ナトリウム	0.5重量%
イオ交換水	残量

## 【0057】実施例8

★整した以外は実施例1と同様にして記録液8を調製した。

下記組成物を用い、pHを水酸化リチウムで7.5に調★

具体例(1-1)の化合物	1.5重量%
具体例(3-1)の化合物	1.0重量%
C. I. ダイレクトブルー199	1.0重量%
チオジエタノール	5重量%
グリセロール	10重量%
一般式(7)においてRがC <sub>10</sub> H <sub>21</sub> 、kが12の界面活性剤	1.5重量%
安息香酸ナトリウム	0.5重量%
イオン交換水	残量

## 【0058】実施例9

☆た以外は実施例1と同様にして記録液9を調製した。

下記組成物を用い、pHを水酸化リチウムで8に調整し☆

具体例(1-1)の化合物	1.5重量%
具体例(1-4)の化合物	1.0重量%
具体例(3-1)の化合物	0.5重量%
2-ピロリドン	5.0重量%
グリセロール	15.0重量%
一般式(8)の界面活性剤(m+n=40)	1.0重量%
具体例(5-2)の界面活性剤	1.0重量%
ペンタクロロフェノールナトリウム	0.2重量%
イオン交換水	残量

## 【0059】実施例10

◆た以外は実施例1と同様にして記録液10を調製した。

下記組成物を用い、pHを水酸化リチウムで8に調整し◆

具体例(1-1)の化合物	1.0重量%
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具体例(3-1)の化合物

具体例(3-5)の化合物

2-ピロリドン

グリセロール

一般式(8)の界面活性剤( $m+n=40$ )

具体例(5-2)の界面活性剤

デヒドロ酢酸ナトリウム

イオン交換水

## 【0060】比較例1

実施例1において具体例(1-1)および(2-1)の化合物に代えてC. I. アシッドブルー249を用いた以外は実施例1と同様にして記録液11を得た。

## 【0061】比較例2

実施例2において具体例(1-1)および(1-4)の化合物に代えてC. I. ダイレクトブルー199を用いた以外は実施例2と同様にして記録液12を得た。

## 【0062】比較例3

実施例3において具体例(4-3)の25%水溶液、スチレンアクリル酸共重合体および一般式(7)の界面活性剤を除き、記録液のpHを4.5とした以外は実施例3と同様にして記録液13を得た。

## 【0063】比較例4

実施例3において一般式(7)の界面活性剤に代えてジ(イソブチル)スルホコハク酸ナトリウムを用いた以外は実施例3と同様にして記録液14を得た。

## 【0064】比較例5

実施例4において具体例(3-1)の化合物に代えてC. I. アシッドブルー1を用いた以外は実施例1と同様にして記録液15を得た。

## 【0065】比較例6

実施例6において具体例(4-7)の25%水溶液および一般式(8)の界面活性剤を除き、水酸化カリウムでpHを8に調整した以外は実施例6と同様にして記録液16を得た。

## 【0066】比較例7

実施例1において具体例(2-1)の化合物に代えてC. I. ダイレクトブルー25を用い、水酸化リチウムを水酸化アンモニウムに代えてpHを調整した以外は実施例1と同様にして記録液17を得た。

【0067】つぎに上記実施例1~10及び比較例1~7によって得られた記録液について、下記のような試験を行った。その結果を表6に示す。

## 1) 画像の鮮明性

サーマルインクジェット方式のノズル径45 $\mu$ m、300dpiのノズルを有するインクジェットプリンター及び積層PZTを液室流路の加圧に使用したノズル径33 $\mu$ m、128のノズルを有するインクジェットプリンターによって、市販の再生紙、上質紙およびボンド紙の3種類の印字用紙に印字を行い、印字画像について、2色重ね部境界のにじみ、画像にじみ、色調、濃度を目視に

30

0.8重量%

0.2重量%

5.0重量%

15.0重量%

2.0重量%

1.0重量%

0.2重量%

残量

より総合的に判断し画像の鮮明性を評価した。表6において、○印は印字された画像の特性が3種類の印字用紙のいずれにおいても満足されている場合を、△印は少なくとも1種の印字用紙で満足されている場合を、×印は3種類の印字用紙のいずれにおいても満足されていない場合を示している。

【0068】また、PVAを主成分とする層を表面に有するPETフィルムに実施例および比較例の記録液を用いて印字すると共に、別に用意したマゼンタ色記録液とイエロー色記録液を用いて重ね印字を行い、その印字画像を有するPETフィルムをオーバーヘッドプロジェクターにより投影し発色性の評価を行った。表6において、○印は透明性が高く、ブルーおよびグリーンの発色が良好である場合を、△印は単色の発色はが良好であるがブルーおよびグリーンの発色がややくすむ場合を、×印は単色でも色ムラやくすむがある場合を示している。

## 【0069】2) 画像の耐水性

印字画像サンプルを30℃の水に1分間浸漬し処理前後の画像濃度の変化をマクベス濃度計で測定し、下記の式により耐水性(退色率%)を求めた。表6において、○印は3種類の印字用紙のいずれにおいても耐水性(退色率%)が20%未満である場合を、△印は20%以上30%未満の場合を、また×印は30%以上である場合を示している。

退色率(%) =  $[1 - (\text{処理後の画像濃度} / \text{処理前の画像濃度})] \times 100$

## 【0070】3) 画像の乾燥性

印字後の画像に一定条件で濾紙を押しつけ記録液が濾紙に転写しなくなるまでの時間を測定した。表6において、3種類の印字用紙のいずれにおいても10秒以内で乾燥した場合を○印とし、それ以上の時間を要した場合を×印として示した。

## 【0071】4) 保存安定性

各記録液をポリエチレン容器に入れ、-20℃、5℃、20℃、70℃のそれぞれの条件下で3カ月保存し、保存後の表面張力、粘度、及び沈殿物析出の有無を調べた。表6において、どの条件で保存しても、物性等の変化がない場合を○印、沈殿はないが物性変化が大きい場合を△印、沈殿の析出が認められる場合を×印として示した。

## 【0072】5) 印字休止時信頼性

ノズル径30 $\mu$ m、128のノズルを有するPZTで駆

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動するヘッドを備えたインクジェットプリンターを使用し、動作中にキャップ、クリーニング等を行わないで印字休止し、どれだけの時間印字休止した場合に印字復帰により噴射方向がずれるか、あるいは吐出液滴の重量が変化するかでその信頼性を評価した。表6において、600秒の印字休止で特に問題のない場合を○印、600\*

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\* 秒の印字休止で液滴重量の変化が小さく、噴射方向のずれが小さい場合を△印、600秒以内の印字休止で顕著な目詰まりが発生した場合を×印として示した。

【0073】

【表6】

	画像の 鮮明性	画像の 耐水性	画像の 乾量性	記録液 保存性	吐出信頼性	OHP 適性
実施例 1	○	○	○	○	○	○
実施例 2	○	○	○	○	○	○
実施例 3	○	○	○	○	○	○
実施例 4	○	○	○	○	○	○
実施例 5	○	○	○	○	○	○
実施例 6	○	○	○	○	○	○
実施例 7	○	○	○	○	○	○
実施例 8	○	○	○	○	○	○
実施例 9	○	○	○	○	○	○
実施例 10	○	○	○	○	○	○
比較例 1	△(註)	×	○	○	○	○
比較例 2	△(註)	△	○	△(註)	△	○
比較例 3	×	○	×	×(註)	×	△
比較例 4	×	○	×	×	△	△
比較例 5	○	×	○	○	○	△
比較例 6	×	○	×	×	×	×
比較例 7	△	△	○	×	△	×

【0074】表6から明らかなように、実施例により得られた記録液を用いた場合には、カラー画像の色再現性に優れ、画像にじみがなく濃度の高い鮮明な画像であり、且つ耐水性に優れた画像をいずれの印字用紙を用いた場合にも得ることができ、また画像の乾燥性にも優れている。さらに、実施例により得られた記録液は、保存安定性に優れており、長期間の保存後においても、また印字休止後においても、吐出信頼性の高いインクジェット記録を行うことができる。

【0075】これに対し、比較例1により得られた記録液では、画像の色調変化が大きく、また画像の耐水性が不十分であり、比較例2により得られた記録液では、画像の色調変化が大きく、画像の耐水性に劣り、また低温において記録液の物性変化が大きいものであった。比較例3、4および6により得られた記録液では、乾燥性不足による濃度むらが発生し画像の鮮明性に劣り、また着色剤の分散安定性が悪く記録液の保存安定性や吐出信頼性に劣るものであった。また、比較例5により得られた記録液では、画像の耐水性が不十分であり、比較例7により得られた記録液では、画像の鮮明性や画像の耐水性が不十分であり、また記録液の保存安定性が悪いものであった。さらに、実施例により得られた記録液を用いた

場合には、OHP適性が良好であったが、比較例3～7により得られた記録液を用いた場合には、OHP適性に劣るものであった。

【0076】

【発明の効果】本発明によれば、シアン色として良好な色調を有しカラー画像の色再現性に優れ、且つ記録画像の耐水性および耐光性に優れた記録液を得ることができる。特に、ブルーとグリーンの色再現性に優れ、オーバーヘッドプロジェクター用透明シートに透明性の優れた画像を形成することができる記録液を得ることができる。本発明によれば、普通紙に形成された記録画像の乾燥性に優れ、且つ画像のにじみが防止され、鮮明な画像を形成することができる記録液を得ることができる。本発明によれば、保存安定性に優れ、長期間の保存後においても、インクジェット記録における吐出信頼性の高い記録液を得ることができる。また、本発明によれば、インクジェット記録における印字休止後の吐出信頼性に優れた記録液を得ることができる。さらに、本発明の記録液を用いるインクジェット記録方法により、耐水性および耐光性に優れ、色再現性が良好で鮮明性に優れたカラー画像を高解像度で形成することができる。



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## (54) MICROCAPSULE INK COMPOSITION FOR INK JET RECORDING AND ITS PRODUCTION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a composition excellent in colorability, light resistance, stably dispersible finely for a long period of time.

**SOLUTION:** Colored resin particles (microcapsule) containing a pigment of an achromatic color such as carbon black, silica, etc., are dispersed into an aqueous medium by a self-water-dispersible resin dyed by a dye such as a self-water-dispersible dyed resin obtained by neutralizing  $\geq 60$ mol % of an acid group of a styrene (meth)acrylic acid copolymer having  $\geq 50$  and  $\leq 280$  acid value to give the objective microcapsule ink composition for ink jet recording.

## CLAIMS

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### [Claim(s)]

[Claim 1] The microcapsule ink constituent for ink jet record characterized by the coloring resin particle (B) to which the endocyst of the achromatic color pigment was carried out with the self-water-dispersion resin (A) which the color dyed distributing water in the aquosity medium (C) used as an indispensable component.

[Claim 2] The microcapsule ink constituent for ink jet record according to claim 1 whose achromatic color pigments are white pigments.

[Claim 3] The microcapsule ink constituent for ink jet record according to claim 2 whose white pigments are at least one sort chosen from a titanium white, a silica, a zinc oxide, and an alumina.

[Claim 4] The microcapsule ink constituent for ink jet record according to claim 1 whose achromatic color pigment is carbon black.

[Claim 5] The microcapsule ink constituent for ink jet record according to claim 4 whose pigment is carbon black and whose colors are a black color and/or a blue color.

[Claim 6] The microcapsule ink constituent for ink jet record according to claim 1 or 5 whose weight ratio of the color to a pigment is 1% – 50% of range.

[Claim 7] the ink jet record according to claim 1 whose self-water-dispersion resin (A) is self-water-dispersion resin with which some [ which has an acid radical / at least ] acid radicals of synthetic resin (1) were neutralized by the base (2) — service water — sex ink.

[Claim 8] Water color ink for ink jet record according to claim 7 whose synthetic resin (1) is the vinyl copolymer which has a carvone acid radical.

[Claim 9] Water color ink for ink jet record according to claim 8 which is at least one monomer chosen from the group which synthetic resin (1) becomes from styrene, permutation styrene, and acrylic ester (meta), and the vinyl copolymer which it is with an acrylic acid (meta).

[Claim 10] The microcapsule ink constituent for ink jet record according to claim 7 whose base (2) is an alcoholic amine.

[Claim 11] The self-water-dispersion coloring resin solution which comes to neutralize some [ which mixed and obtained the synthetic resin (1) which can carry out self-moisture powder by neutralization, and which has an acid radical, the base (2) which may neutralize said acid radical, the color (3), and the achromatic color pigment (4) under existence of an organic solvent (5) / at least ] acid radicals of this resin (1), Mix the aquosity medium (C) which uses water as an indispensable component, perform phase inversion emulsification, and the coloring resin particle (B) which connoted the achromatic color pigment (4) by the self-water-dispersion resin (A) which the color (3) dyed is distributed in an aquosity medium (C). Subsequently, the manufacture approach of the microcapsule ink constituent for ink jet record characterized by removing said organic solvent (5) from the obtained aquosity dispersion liquid.

[Claim 12] The manufacture approach of the water color ink for ink jet record according to claim 11 that synthetic resin (1) is the vinyl copolymer which has a carvone acid radical.

[Claim 13] The manufacture approach of the water color ink for ink jet record according to claim 12 which is at least one monomer chosen from the group which synthetic resin (1) becomes from styrene, permutation styrene, and acrylic ester (meta), and the vinyl copolymer which it is with an acrylic acid (meta).

[Claim 14] The manufacture approach of the microcapsule ink constituent for ink jet record according to claim 11 that a base (2) is an alcoholic amine.

## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the microcapsule ink constituent for ink jet record to which an achromatic color pigment is characterized by coming to contain the coloring resin particle by which endocyst was carried out as a microcapsule component with the self-water-dispersion resin which the color dyed in more detail, and its manufacture approach about the microcapsule ink constituent for ink jet record, and its manufacture approach.

[0002]

[Description of the Prior Art] Among the conventional ink for ink jet record, although high coloring was obtained, as for color ink, a deck watertight luminaire and lightfastness had the fault that a blot of the alphabetic character in printing was bad large. On the other hand, although pigment ink had the good blot of a deck watertight luminaire, lightfastness, and an alphabetic character, coloring of a color had the fault that it was bad as compared with color ink. Moreover, generally, since the pigment currently used in black ink was carbon black, it could not but become the hue which turned reddish-brown a little.

[0003] In order to solve the above-mentioned fault, the proposal of coloring a polymer particle with a color is made. As an example The ink constituent containing the urethane polymer latex which contained the color in JP,58-45272,A, In JP,62-95366,A, the adjustment approach of the ink jet constituent containing the color by which dissolved a polymer and fat dye into the water-insoluble nature organic solvent, evaporated the solvent after mixing with the water solution which contains a surface active agent further and making it emulsify, and endocyst was carried out into the polymer particle is proposed. However, since there was no core material, it had the fault of being hard to obtain the coloring particle which was excellent in distributed stability with the particle. Moreover, since the polymer was colored using a color, it did not necessarily excel in lightfastness.

[0004] On the other hand, although the ink for image recording which makes a color or a pigment stick to the front face of an emulsion particle was proposed in JP,3-160069,A, property degradation in which non-adsorbed dyes and pigments originate in dyes and pigments, such as bleeding, mostly was not avoided.

[0005]

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is to offer the microcapsule ink constituent for ink jet record which was excellent in color enhancement and lightfastness, and was excellent in distributed stability with the particle.

[0006]

[Means for Solving the Problem] this invention person etc. came to solve this invention, as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem.

[0007] That is, this invention has the coloring resin particle (B) to which the endocyst of the achromatic color pigment was carried out with the self-water-dispersion resin (A) which the color dyed in offering the microcapsule ink constituent for ink jet record characterized by distributing water in the aquosity medium (C) used as an indispensable component.

[0008] Moreover, self-moisture powder of this invention can be carried out by neutralization. The self-water-dispersion coloring resin solution which comes to neutralize some [ which mixed and obtained the synthetic resin (1) which has an acid radical, the base (2) which may neutralize said acid radical, the color (3), and the achromatic color pigment (4) under existence of an organic solvent (5) / at least ] acid

radicals of this resin (1), Mix the aqueous medium (C) which uses water as an indispensable component, perform phase inversion emulsification, and the coloring resin particle (B) which contained the achromatic color pigment (4) by the self-water-dispersion resin (A) which the color (3) dyed is distributed in an aqueous medium (C). Subsequently, it is in offering the manufacture approach of the microcapsule ink constituent for ink jet record characterized by removing said organic solvent (5) from the obtained aqueous dispersion liquid.

[0009] The self-water-dispersion resin in which self-water-dispersion is shown by neutralization and with which some of acid radicals [ at least ] concerned were neutralized by the base (2) in the synthetic resin (1) which has an acid radical is used for the self-water-dispersion resin (A) which forms the microcapsule in this invention, and the husks material resin of the so-called microcapsule. Such resin is good, and compatibility with a color also has good \*\*\*\* with an achromatic color pigment, and it is desirable.

[0010] Although it is especially a carboxylic-acid radical, a sulfonic group, a sulfinic-acid radical, etc. as an acid radical which synthetic resin (1) has and is not limited, a carboxylic-acid radical is common.

[0011] As for the acid number of the synthetic resin (1) concerned, 280 or less [ 50 or more ] are desirable. The moisture powder stability of the coloring resin particle obtained when the acid number of synthetic resin (1) was less than 50 is not enough. Moreover, it is easy to produce condensation in the case of neutralization by the base of the water-dispersion resin which dissolved in the organic solvent when the acid number exceeded 280. Moreover, the acid number of the synthetic resin (1) used from it being easy to produce nozzle blinding when it adds in water, and some resin dissolves is or more 50 280 or less range, and the range of it is 70-250 preferably.

[0012] As such synthetic resin (1), the vinyl copolymer which has a carboxylic-acid radical is good. For example, styrene or permutation styrene like alpha methyl styrene, Acrylic-acid methyl ester, ethyl-acrylate ester, butyl acrylate ester, Acrylic ester, such as 2-ethylhexyl acrylate ester, methacrylic acid methylester, At least one or more monomeric units chosen from methacrylic ester, such as ethyl methacrylate ester, methacrylic-acid butyl ester, and 2-ethylhexyl methacrylate, A vinyl copolymer including at least one or more monomeric units chosen from an acrylic acid and a methacrylic acid is a vinyl copolymer using a styrene monomer, an acrylic-acid monomer, and a methacrylic acid monomer as an indispensable monomer component desirable still more preferably. Since the vinyl copolymer using these monomers does not have in the molecular structure, the radical, for example, the ester bond etc., etc. which is easy to be divided with light, heat, a solvent, etc., it can be said to be very stable resin. Especially, when such indispensable monomer component percentage is 5-25 mol % of 5-15 mol % and methacrylic acid monomers of 60-90 mol % and acrylic-acid monomers of styrene monomers, the outstanding coloring resin particle (coloring microcapsule particle) which does not have nozzle blinding as an object for ink jet record is made possible.

[0013] Although there is especially no limit also about the molecular weight range of the above mentioned synthetic resin (1), the thing of or more 1000 100,000 or less molecular weight is more desirable. Of course, as long as this resin (1) forms a stable microcapsule in combination with the aqueous medium (C) which carries out a postscript, it is not limited to especially these, and two or more kinds may be mixed and used for coincidence.

[0014] Moreover, even if the glass transition temperature of the synthetic resin (1) concerned is less than 50 degrees C, fixable [ of the alphabetic character after printing to the recording paper ] is good, but if it takes into consideration raising nozzle blinding and storage stability further, glass transition temperature is desirable and 50 degrees C or more of things 60 degrees C or more are more preferably suitable as an object

for ink jet record.

[0015] It is necessary to neutralize to extent which synthetic resin (1) does not dissolve in water, and as long as neutralization by the base (2), i.e., the neutralization by the alkaline neutralizer, is extent which is not dissolved, it may add a base (2) superfluously. It is desirable to neutralize more than 60 mol % of the acid radical of synthetic resin (1). The coloring resin particle (B) obtained as a neutralization index is more than 60 mol % is a particle, and excellent in distributed stability.

[0016] Although it will not be specified especially if the effectiveness in this invention is attained as a content in the inside of the aqueous medium (C) of this self-water-dispersion resin (A), an amount which becomes 0.5 – 20 % of the weight in the water-color-ink constituent finally obtained is desirable.

[0017] Especially as a base (2), although alcoholic amines, such as triethanolamine, diethanolamine, and N-methyldiethanolamine, are usable, for example besides alkalis, such as a hydroxide of alkali metal, such as a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, ammonia, triethylamine, and a morpholine, especially use of an alcoholic amine is desirable. The ink for ink jet record in which it excelled more than it was an alcoholic amine in the distributed stability of a coloring resin particle (B), and the nozzle blinding by the particle condensation accompanying evaporation of moisture or an organic solvent was improved is obtained.

[0018] What is necessary is just to choose the best conditions about the adoption, although there are whether it adding in an aqueous medium and an approach in case the organic solvent solution and aqueous medium (C) of whether it adds in the organic solvent solution of synthetic resin (1) beforehand and this synthetic resin (1) are mixed as an approach of adding the base (2) concerning the synthetic resin (1) which has the acid radical used by this invention, and neutralizing.

[0019] On the other hand, the pigment used in this invention is a pigment of an achromatic color, a black pigment and white pigments are one of such things, and carbon black also includes extenders, such as a silica besides a titanium white, a zinc oxide, and an alumina, in this by this invention as white pigments as a black pigment. In the case of the above mentioned white pigments, generally it remains as it is and is used, but a color may be used for said white pigments with the gestalt of the color pigment which carried out surface adsorption depending on the need.

[0020] Moreover, as a color, although there is especially no limit, the desirable color which can dissolve in an organic solvent is good. Although azo dye, such as for example, monoazo JISUAZO, metal complex dye, naphthol dye, anthraquinone dye, an indigo color, a carbonium pigment, a kino imine color, cyanine dye, quinoline dye, nitro dye, nitroso dye, a benzoquinone color, a naphthoquinone color, the North America Free Trade Agreement RUIMIDO color, a peri non color, phthalocyanine dye, a triaryl methane system, etc. can be illustrated as a typical thing, it is not limited to these examples. Although a part of these colors may exist in the form which carries out powder, it is desirable to choose what is dissolved in the husks material resin which forms the microcapsule.

[0021] In the microcapsule in this invention, these achromatic color pigment and a color exist with the self-water-dispersion resin which the color dyed as a coloring resin particle to which the endocyst of the achromatic color pigment was carried out. coloring of a color which a water resisting property and whose lightfastness are moreover good, and does not have a blot of an alphabetic character by this coloring resin particle (coloring microcapsule particle) being excellent in distributed stability is good — etc. — effectiveness is also demonstrated. Furthermore, various usefulness is shown also from the point of color.

[0022] For example, unlike coloring of different-species pigments, there is little mixture of a unique particle, there is no color separation of printed matter, compared with coloring which tends to sink only with a pigment, the color-enhancing amelioration

effectiveness is acquired according to concomitant use of a color, and only with a color, although it is weak to lightfastness, there is an advantage that lightfastness improves sharply according to dispersion and the absorption effect of ultraviolet rays, according to concomitant use of a pigment. Furthermore, when it is an extender with a refractive index [ like a silica or an alumina ] small again whose achromatic color pigment of a core material is, transparency is high and transparent and bright coloring is obtained with the self-water-dispersion resin which the color dyed. An advantage — bright and high coloring of concealment nature is obtained with the self-water-dispersion resin with which the color dyed the white pigments with a large refractive index like a titanium white — is mentioned. On the other hand, when a core material is carbon black of a black pigment, as for dyeing by the color, toning can be set as the main purpose. By carbon black, especially a pigment becomes reproducible [ the hue of \*\*\*\* with a high-class feeling which is not in conventional carbon black ], in [ whose colors are a black color and/or a blue color ] combining.

[0023] Although the amount of the total used of a color and an achromatic color pigment used in this invention will not be specified especially if the effectiveness in this invention is attained, its amount which becomes 0.5 – 20 % of the weight in the water color ink finally obtained is desirable. In order to attain the effectiveness in this invention, as for the weight ratio of the color to an achromatic color pigment, it is desirable to use in the range below 1-% of the weight or more 50% weight.

[0024] the coloring microcapsule in this invention dyes with a color the resin particle (microcapsule particle) which microencapsulates this pigment and which connoted this pigment, after dyeing resin with the color which performs dyeing of the resin by the color, simultaneously microencapsulation of an achromatic color pigment — it is formed by the means of \*\*.

[0025] this invention constituent containing the formed coloring microcapsule component, i.e., the constituent for ink jet record of this invention which distributed the coloring microcapsule to which the endocyst of the achromatic color pigment was carried out with the self-water-dispersion resin which the color dyed in the aquosity medium For example, a color and an achromatic color pigment are added in the organic solvent solution of synthetic resin (1), and after performing the dissolution and distribution using an agitator or distributed equipment and mixing, it can prepare by mixing it and an aquosity solvent (C) under existence of a base (2).

[0026] If it explains more concretely, the microcapsule ink constituent for ink jet record of this invention can be easily manufactured by preparing by the microencapsulation approach generally called the phase inversion emulsifying method. The manufacture by the phase inversion emulsifying method is fundamentally meltable to an organic solvent as the 1st step, and synthetic resin (1) is dissolved for self-water-dispersion in an organic solvent by neutralization. Furthermore, by mixing the solution with the aquosity medium of an excessive amount under existence of a base (2) as the process (mill base process) which distributes an achromatic color pigment and a color in the resin solution concerned, and is dissolved, and the 2nd step It may consist of a process (capsulation process) which obtains the resin particle which connoted the achromatic color pigment with the water-dispersion resin which the color dyed, and the process (desolventization process) which removes the organic solvent used at the mill base process of the 1st step as the 3rd step by the case may be put in.

[0027] It is desirable that you make it distribute or dissolve into self-water-dispersion resin before a color and an achromatic color pigment distribute both in an aquosity medium beforehand on the occasion of manufacture of the aforementioned microcapsule ink constituent.

[0028] When encapsulating using said phase inversion emulsifying method, the organic solvent used in the 1st step Moreover, an acetone, Ketones, such as dimethyl ketone

and a methyl ethyl ketone; A methanol, Alcohols solvents, such as ethanol and isopropyl alcohol; A tetrahydrofuran, Ethers solvents, such as dioxane; Chlorine-based solvent; benzene, such as chloroform and a methylene chloride, aromatic solvent [, such as toluene, ]; — ester solvent [, such as ethyl-acetate ester, ], although they are usable if glycol ether system solvent; amides, such as ethylene glycol monomethyl ether and ethylene glycol wood ether, dissolve resin In the case of the phase inversion emulsifying method using said synthetic resin (1), at least one or more kinds of combination chosen from ketones and an alcohols solvent gives a good microcapsule, and this combination is suitable.

[0029] In this invention, additives, such as a dispersant, a plasticizer, an antioxidant, and an ultraviolet ray absorbent, may be used with an organic solvent, resin, a color, and a pigment if needed. The 2nd-step capsulation mixes a color and an achromatic color pigment with resin to the above-mentioned solvent, performs the dissolution and distribution using an agitator or distributed equipment, and is performed by mixing the aqueous medium which uses the obtained organic solvent solution and water as an indispensable component.

[0030] Although encapsulated by mixing water or a water solution under existence of a base (2) at the mill base obtained in the 1st step in the 2nd-step microencapsulation, since loose condensation of capsules may be produced depending on the achromatic color pigment and color to be used, it is desirable to add water or a water solution and to perform mixed distribution after capsulation. Although the coloring solution which contains self-water-dispersion resin in the aqueous medium which uses water as an indispensable component may be added at this process, it is desirable at the point that aqueous dispersion liquid with more uniform particle diameter [ add / into the coloring solution which contains the resin concerned conversely / an aqueous medium ] are obtained. A surfactant can be used together depending on the need, and it can be made to be able to emulsify compulsorily, and can also obtain. However, not using, since a surfactant and protective colloid have the inclination to reduce the physical properties of the particle finally obtained is liked.

[0031] A base (2) is added in the mill base or a water solution. Moreover, the water used in an aqueous medium has the desirable grade more than ion exchange water. as the 3rd step, after capsulation is completed, the water dispersion pressed down and stabilized obtains swelling and condensation of a coloring microcapsule by passing through the desolventization process which removes the organic solvent which dissolves the synthetic resin (1) used at the mill base process of the 1st step — having — this — ink jet record — service water — it is suitable for sex ink. Water may be removed as long as it is required in this deliquoring process. Moreover, of course, this process of the 3rd step may be skipped depending on the case.

[0032] In order to present practical use by using a coloring microcapsule \*\*\*\* this invention constituent as the ink constituent for ink jet record, it is desirable to use the water-soluble organic solvent for desiccation prevention as an additive. There are pyrrolidones, such as polyhydric alcohol, such as the ethylene glycol and propylene glycol which are conventionally known as a desiccation inhibitor, a diethylene glycol, dipropylene glycol, a polyethylene glycol, a polypropylene glycol, and a glycerol, or those alkyl ether, a N-methyl-2-pyrrolidone, and 2-pyrrolidone, amides, dimethyl sulfoxide, imidazolidinone, etc., and it is not limited to these.

[0033] Moreover, the water-soluble organic solvent for permeability grant may be added if needed, and although glycol ether, such as lower alcohol, such as ethanol and isopropyl alcohol, and diethylene-glycol-N-butyl ether, etc. can be used, it is not limited to these. In addition, additives, such as a surfactant for osmosis on water soluble resin, pH regulator, and distribution, defoaming and paper, antiseptics, and a chelating agent, can be added if needed.

[0034] It is better to avoid addition of the additive after the last filtration preferably,



although these additives can be added at the suitable process from the 1st step to a culmination. After adjustment of the last presentation is completed, it is desirable to remove a large drop radial ball child by filter filtration, centrifugal separation, etc., and to consider as the water color ink of this invention.

[0035]

[Embodiment of the Invention] It is as follows, when the case where the gestalt of suitable operation of this invention is manufactured by the phase inversion emulsifying method is made into an example and it explains.

[0036] The color which the acid number obtained by \*\*\*\*(ing) at least one monomer chosen from the group which consists of styrene, permutation styrene, and acrylic ester (meta) as synthetic resin, and acrylic acid (meta) may dissolve in said synthetic resin as the synthetic-resin solution with which or more 50 with 280 or less and an or more 1000 molecular weight [ or less 100,000 ] vinyl copolymer was dissolved in the organic solvent, an achromatic color pigment, and a color is mixed and milled, and the coloring mill base is obtained. Let the weight ratio of the color to a pigment be the range below 1-% of the weight or more 50% weight. The water dispersion of the coloring microcapsule which the coloring resin particle to which the endocyst of the achromatic color pigment was carried out with the self-water-dispersion resin which the color dyed distributed in the aquosity medium is obtained by adding the base which may neutralize the acid radical of said synthetic resin to this coloring mill base, carrying out stirring mixing, dropping the aquosity medium which contains water under stirring further, mixing, and performing phase inversion emulsification. Under the present circumstances, the addition of the base as anti-alkali makes the range the amount which neutralizes more than 60 mol % of an acid radical. When loose condensation of capsules is produced by the achromatic color pigment and color to be used, additional mixing of water or the water solution is carried out after capsulation, and it distributes again. Vacuum distillation is performed, the organic solvent furthermore used for the dissolution of synthetic resin is removed, and the ink constituent for ink jet record is obtained.

[0037]

[Example] Next, an example and the example of a comparison are given and this invention is explained still more concretely. In addition, the "section" in the following examples expresses the "weight section."

[0038] (Example 1)

Carbon black 20 section styrene acrylic acid resin The 20 sections (styrene / 2-ethylhexyl acrylate / acrylic-acid =77/10/13; acid number 100, molecular weight 40,000)

Oily phthalocyanine dye 2 section methyl ethyl ketone The compound of the 49 sections is milled with a paint shaker for 4 hours using a glass bead with a diameter of 0.2mm, and it is a methyl ethyl ketone. 40 section isopropyl alcohol The 40 sections were added, contents were taken out and the mill base solution 171 section was obtained.

[0039] Adding and stirring the triethanolamine 5.3 section (about 100% of neutralization indices of resin) in said mill base 171 section, the mixed liquor of the glycerol 50 section and the ion-exchange-water 120 section was dropped at the rate of 5ml/m, and the coloring microcapsule constituent was obtained. Distributed processing was again performed for the obtained coloring microcapsule constituent by the pressure of 1500kg/cm<sup>2</sup> using the collision type distribution equipment nano mizer (nano mizer incorporated company make). After the mixed liquor of the glycerol 80 section and the ion-exchange-water 300 section was dropped at the obtained processing liquid at the rate of 5ml/m, a methyl ethyl ketone and isopropyl alcohol were distilled off using the rotary evaporator, and the last coloring microcapsule water distribution object was obtained.

[0040] It filtered using 1.5-micrometer filter and this water distribution object was used as the microcapsule ink for ink jet record. There is also no aggregate, stable distribution was shown over the long period of time, printing using an ink jet printer was stable, the microcapsule in the obtained ink has the mean particle diameter of 0.1 micrometers, and it was [ the obtained printed matter has the color tone of \*\*\*\*, does not have a blot, either and ] excellent in waterproof lightfastness.

[0041] (Example 1 of a comparison) The microcapsule ink for ink jet record was similarly obtained by the combination excluding oily phthalocyanine dye from the mill base of an example 1. The obtained printed matter wore brown a little, and was not able to say it as a good color tone.

[0042] (Example 2)

Colloidal silica 2 section styrene acrylic acid resin The 40 sections (styrene / 2-ethylhexyl acrylate / acrylic-acid / methacrylic acid =72/5/10/13; acid number 155, molecular weight 45,000)

Oily Magenta color 4 section methyl ethyl ketone 50 section glass bead The compound of the 150 sections is milled with a paint shaker for 4 hours, and it is a methyl ethyl ketone. 40 section isopropyl alcohol The 40 sections were added, contents were taken out and the mill base solution 176 section was obtained.

[0043] Adding and stirring the triethanolamine 16.5 section (about 100% of neutralization indices of resin) in said mill base 176 section, the mixed liquor of the glycerol 65 section and the ion-exchange-water 210 section was dropped at the rate of 5ml/m, and the coloring microcapsule constituent was obtained.

[0044] Distributed processing was again performed for the obtained coloring microcapsule liquid which was obtained by the pressure of 1500kg/cm<sup>2</sup> using the collision type distribution equipment nano mizer (nano mizer incorporated company make). After the mixed liquor of the glycerol 75 section and the ion-exchange-water 210 section was dropped at the obtained processing liquid at the rate of 5ml/m, a methyl ethyl ketone and isopropyl alcohol were distilled off using the rotary evaporator, and the last coloring microcapsule water distribution object was obtained.

[0045] It filtered using 1.5m filter and this water distribution object was used as the microcapsule ink constituent for ink jet record. There is also no aggregate, stable distribution was shown over the long period of time, printing using an ink jet printer was stable, the microcapsule in the obtained ink has the mean particle diameter of 0.086 micrometers, and it was [ the obtained printed matter has the color tone of a bright Magenta color, does not have a blot, either, and ] excellent in waterproof lightfastness.

[0046] (Example 2 of a comparison)

Styrene acrylic acid resin The 40 sections (styrene / 2-ethylhexyl acrylate / acrylic-acid / methacrylic acid =72/5/10/13; acid number 155, molecular weight 45,000)

Oily Magenta color 4 section methyl ethyl ketone 90 section isopropyl alcohol The compound excluding colloidal silica from combination of the example 2 of the 40 sections was dissolved with the agitator, and the mill base solution 174 section was obtained.

[0047] Adding and stirring the triethanolamine 16.5 section (about 100% of neutralization indices of resin) in said mill base 174 section, the mixed liquor of the glycerol 65 section and the ion-exchange-water 210 section was dropped at the rate of 5ml/m, and the coloring resin emulsification object was obtained.

[0048] Distributed processing was again performed for the obtained coloring resin emulsification object which was obtained by the pressure of 1500kg/cm<sup>2</sup> using the collision type distribution equipment nano mizer (nano mizer incorporated company make). After the mixed liquor of the glycerol 75 section and the ion-exchange-water 210 section was dropped at the obtained processing liquid at the rate of 5ml/m, a methyl ethyl ketone and isopropyl alcohol were distilled off using the rotary evaporator,

and the last coloring resin emulsification object was obtained. Filtration could not do 5m filter, either and, as for this coloring resin emulsification object, the microcapsule ink constituent for ink jet record was not obtained. Although the coloring resin emulsification object had the mean particle diameter of 0.22 micrometers, about 2% of big and rough particles 1 micrometers or more existed.

[0049] (Example 3) The microcapsule ink constituent for ink jet record was prepared by the same approach as an example 2 except using the triethanolamine of the amount which replaces with the styrene acrylic resin of an example 2, and is further equivalent to 100% of neutralization indices of the resin concerned using styrene acrylic acid resin (styrene / acrylic-acid / methacrylic acid =65/10/25; acid number 221, molecular weight 45,000). There is also no aggregate, stable distribution was shown over the long period of time, printing using an ink jet printer was stable, the microcapsule in the obtained ink has the mean particle diameter of 0.060 micrometers, and it was [ the obtained printed matter has the color tone of a bright Magenta color, does not have a blot, either, and ] excellent in waterproof lightfastness.

[0050]

[Effect of the Invention] The microcapsule ink constituent for ink jet record of this invention which the coloring resin particle which connoted the achromatic color pigment by the self-water-dispersion resin which the color dyed distributed in the aquosity medium (C) has the outstanding color enhancement and lightfastness, and enables stable distribution over a long period of time.

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(54)【発明の名称】 インクジェット記録用マイクロカプセルインク組成物及びその製造方法

(57)【要約】

【解決手段】 染料で染色された自己水分散性樹脂、例えば酸価が50以上280以下のスチレン(メタ)アクリル酸共重合体の酸基の60モル%以上が中和された自己水分散性の染色樹脂によって、カーボンブラック、シリカ等の無彩色顔料が内包された着色樹脂粒子(マイクロカプセル)が、水性媒体中に分散したインクジェット記録用マイクロカプセルインク組成物。

【効果】 本発明のインクジェット記録用マイクロカプセルインクは、優れた発色性、耐光性を有し、また長期にわたって安定な微分散を可能にする。

(2)

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## 【特許請求の範囲】

【請求項1】 染料が染着した自己水分散性樹脂（A）によって無彩色顔料が内包された着色樹脂粒子（B）が、水を必須成分とする水性媒体（C）中に分散していることを特徴とするインクジェット記録用マイクロカプセルインク組成物。

【請求項2】 無彩色顔料が、白色顔料である請求項1記載のインクジェット記録用マイクロカプセルインク組成物。

【請求項3】 白色顔料が、チタンホワイト、シリカ、酸化亜鉛、アルミナから選ばれる少なくとも1種である請求項2記載のインクジェット記録用マイクロカプセルインク組成物。

【請求項4】 無彩色顔料が、カーボンブラックである請求項1記載のインクジェット記録用マイクロカプセルインク組成物。

【請求項5】 顔料がカーボンブラックであり、染料が黒色染料及び／又は青色染料である請求項4記載のインクジェット記録用マイクロカプセルインク組成物。

【請求項6】 顔料に対する染料の重量比率が、1%～50%の範囲である請求項1または5記載のインクジェット記録用マイクロカプセルインク組成物。

【請求項7】 自己水分散性樹脂（A）が、酸基を有する合成樹脂（1）の少なくとも一部の酸基が塩基（2）で中和された自己水分散性樹脂である請求項1記載のインクジェット記録用水性インク。

【請求項8】 合成樹脂（1）が、カルボン酸基を有するビニル共重合体である請求項7記載のインクジェット記録用水性インク。

【請求項9】 合成樹脂（1）が、スチレン、置換スチレン、（メタ）アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、（メタ）アクリル酸とのビニル共重合体である請求項8記載のインクジェット記録用水性インク。

【請求項10】 塩基（2）が、アルコールアミンである請求項7記載のインクジェット記録用マイクロカプセルインク組成物。

【請求項11】 中和により自己水分散しうる、酸基を有する合成樹脂（1）と前記酸基を中和しうる塩基（2）と染料（3）と無彩色顔料（4）とを有機溶剤（5）の存在下に混合して得た該樹脂（1）の少なくとも一部の酸基を中和してなる自己水分散性の着色樹脂溶液と、水を必須成分とする水性媒体（C）とを混合して転相乳化を行い、染料（3）が染着した自己水分散性樹脂（A）で無彩色顔料（4）を内包した着色樹脂粒子（B）を水性媒体（C）中に分散させ、次いで得られた水性分散液から前記有機溶剤（5）を除去することを特徴とするインクジェット記録用マイクロカプセルインク組成物の製造方法。

【請求項12】 合成樹脂（1）が、カルボン酸基を有するビニル共重合体である請求項11記載のインクジェツ

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ト記録用水性インクの製造方法。

【請求項13】 合成樹脂（1）が、スチレン、置換スチレン、（メタ）アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、（メタ）アクリル酸とのビニル共重合体である請求項12記載のインクジェット記録用水性インクの製造方法。

【請求項14】 塩基（2）が、アルコールアミンである請求項11記載のインクジェット記録用マイクロカプセルインク組成物の製造方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はインクジェット記録用マイクロカプセルインク組成物及びその製造方法に関し、更に詳しくは、染料が染着した自己水分散性樹脂によって無彩色顔料が内包された着色樹脂粒子をマイクロカプセル成分として含んでなることを特徴とするインクジェット記録用マイクロカプセルインク組成物及びその製造方法に関するものである。

【0002】

【従来の技術】従来のインクジェット記録用インクのうち、染料インクは高い発色が得られるが、耐水・耐光性が悪くかつ印刷における文字の滲みが大きいという欠点を有していた。一方顔料インクは、耐水・耐光性・文字の滲みが良好であるが、カラーの発色が染料インキと比較して悪いという欠点を有していた。また黒色インクで使用している顔料は一般的にはカーボンブラックであるため、やや赤茶けた色相にならざるを得なかった。

【0003】上記欠点を解決するために、ポリマー粒子を染料で着色するという提案がなされており、具体例としては、特開昭58-45272号公報では染料を含有したウレタンポリマーラテックスを含むインク組成物、特開昭62-95366号公報では水不溶性有機溶媒中にポリマーと油性染料を溶解し、さらに表面活性剤を含む水溶液と混合して乳化させた後に溶媒を蒸発してポリマー粒子中に内包された染料を含むインクジェット組成物の調整方法が提案されている。しかし芯材がないことから微粒子で分散安定性に優れた着色粒子が得にくいという欠点を有していた。またポリマーを染料を用いて着色しているため、必ずしも耐光性に優れていなかった。

【0004】一方、特開平3-160069号公報では、エマルジョン粒子の表面に染料または顔料を吸着させる画像記録用インクが提案されているが、未吸着の顔料が多くブリード等の染顔料に起因する特性劣化が避けられなかった。

【0005】

【発明が解決しようとする課題】本発明が解決しようとする課題は、発色性、耐光性に優れ、また微粒子で分散安定性に優れたインクジェット記録用マイクロカプセルインク組成物を提供することにある。

【0006】

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【課題を解決するための手段】本発明者等は、上記の課題を解決するために鋭意研究を重ねた結果、本発明を解決するに至った。

【0007】即ち本発明は、染料が染着した自己水分散性樹脂（A）によって無彩色顔料が内包された着色樹脂粒子（B）が、水を必須成分とする水性媒体（C）中に分散していることを特徴とするインクジェット記録用マイクロカプセルインク組成物を提供するにある。

【0008】また本発明は、中和により自己水分散性樹脂（A）と前記酸基を中和する塩基（2）と染料（3）と無彩色顔料（4）とを有機溶剤（5）の存在下に混合して得た該樹脂（1）の少なくとも一部の酸基を中和してなる自己水分散性の着色樹脂溶液と、水を必須成分とする水性媒体（C）とを混合して転相乳化を行い、染料（3）が染着した自己水分散性樹脂（A）で無彩色顔料（4）を内包した着色樹脂粒子（B）を水性媒体

（C）中に分散させ、次いで得られた水性分散液から前記有機溶媒（5）を除去することを特徴とするインクジェット記録用マイクロカプセルインク組成物の製造方法を提供するにある。

【0009】本発明においてマイクロカプセルを形成している自己水分散性樹脂（A）、いわゆるマイクロカプセルの殻材樹脂には、中和により自己水分散性を示す、酸基を有する合成樹脂（1）において当該酸基の少なくとも一部が塩基（2）で中和された自己水分散性樹脂を用いる。このような樹脂は無彩色顔料との濡れが良く、かつ染料との相溶性も良好で好ましい。

【0010】合成樹脂（1）が有する酸基としてはカルボン酸基、スルホン酸基、スルフィン酸基等であって特に限定されるものではないが、このうちカルボン酸基が一般的である。

【0011】当該合成樹脂（1）の酸価は50以上280以下が好ましい。合成樹脂（1）の酸価が50未満の時は得られた着色樹脂粒子の水分散安定性が十分ではなく、また酸価が280を越える場合には有機溶媒に溶解した水分散性樹脂の塩基による中和の際に凝集を生じ易く、また水に添加した際に一部の樹脂が溶解することによってノズル目詰まりを生じ易いことから、用いる合成樹脂（1）の酸価は、50以上280以下の範囲で、好ましくは70～250の範囲である。

【0012】このような合成樹脂（1）としては、カルボン酸基を有するビニル共重合体がよく、例えばスチレンあるいは $\alpha$ -メチルスチレンのような置換スチレン、アクリル酸メチルエステル、アクリル酸エチルエステル、アクリル酸ブチルエステル、アクリル酸2-エチルヘキシルエステル等のアクリル酸エステル、メタクリル酸メチルエステル、メタクリル酸エチルエステル、メタクリル酸ブチルエステル、メタクリル酸2-エチルヘキシル等のメタクリル酸エステルから選ばれる少なくとも一つ

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選ばれる少なくとも一つ以上のモノマー単位を含むビニル共重合体为好ましく、さらに好ましくは必須モノマー成分としてスチレンモノマー、アクリル酸モノマー、メタアクリル酸モノマーを用いるビニル共重合体である。これらのモノマーを用いたビニル共重合体はその分子構造中に、光、熱、溶剤等によって分断され易い基例えばエステル結合等を有していないので極めて安定な樹脂と言える。特にこれらの必須モノマー成分構成比率がスチレンモノマー60～90モル%、アクリル酸モノマー5～15モル%、メタアクリル酸モノマー5～25モル%である場合にはインクジェット記録用としてノズル目詰まりのない優れた着色樹脂粒子（着色マイクロカプセル粒子）を可能とする。

【0013】前記した合成樹脂（1）の分子量範囲についても特に制限はないが、1000以上10万以下の分子量のものがより好ましい。勿論、かかる樹脂（1）が後記する水性媒体（C）との組み合わせで安定なマイクロカプセルを形成するものであれば、これらに特に限定されるものではなく、同時に2種類以上を混合して使用しても良い。

【0014】また当該合成樹脂（1）のガラス転移温度は、50℃未満であっても記録紙への印刷後の文字の定着性は良好であるが、ノズル目詰まりや貯蔵安定性を更に高めることを考慮するとガラス転移温度が好ましくは50℃以上、より好ましくは60℃以上のものがインクジェット記録用として好適である。

【0015】塩基（2）による中和、即ちアルカリ性中和剤による中和は、合成樹脂（1）が水に溶解しない程度に中和する必要があり、溶解しない程度であれば塩基（2）を過剰に加えても良い。合成樹脂（1）の酸基の60モル%以上を中和するのが好ましい。中和率が60モル%以上であると、得られる着色樹脂粒子（B）は微粒でかつ分散安定性に優れている。

【0016】かかる自己水分散性樹脂（A）の水性媒体（C）中での含有量としては、本発明における効果を達成すれば特に規定されないが、最終的に得られる水性インク組成物中で0.5～20重量%となるような量が好ましい。

【0017】塩基（2）としては、例えば水酸化ナトリウム、水酸化カリウム、水酸化リチウム等のアルカリ金属の水酸化物、アンモニア、トリエチルアミン、モルホリン等の塩基性物質の他、特にトリエタノールアミン、ジエタノールアミン、N-メチルジエタノールアミン等のアルコールアミンが使用可能であるが、特にアルコールアミンの使用が好ましい。アルコールアミンであると、より着色樹脂粒子（B）の分散安定性に優れ、また水分や有機溶剤の蒸発に伴う粒子凝集によるノズル目詰まりが改良されたインクジェット記録用インクが得られる。

【0018】本発明で使用される酸基を有する合成樹脂（1）にかかる塩基（2）を添加して中和する方法としては、

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予め合成樹脂 (I) の有機溶媒溶液に添加するか、該合成樹脂 (I) の有機溶媒溶液と水性媒体 (C) とを混合する際に水性媒体中に添加するか等の方法があるが、その採用については最も良い条件を選択すればよい。

【0019】一方、本発明において用いる顔料は無彩色の顔料であって、このようなものとしては黒色顔料、白色顔料があり、黒色顔料としてはカーボンブラックが、白色顔料としては、チタンホワイトのほかシリカ、酸化亜鉛、アルミナ等の体質顔料も本発明ではこの中に包含する。前記した白色顔料の場合、一般的にはそのまま使用されるが、必要によっては前記白色顔料に染料を表面吸着させた着色顔料の形態にて用いてもよい。

【0020】また染料としては、特に制限はないが、好ましくは有機溶剤に溶解可能な染料がよい。代表的なものとして例えばモノアゾ・ジスアゾ等のアゾ染料、金属錯塩染料、ナフトール染料、アントラキノン染料、インジゴ染料、カーボニウム染料、キノイミン染料、シアニン染料、キノリン染料、ニトロ染料、ニトロソ染料、ベンゾキノン染料、ナフトキノン染料、ナフタルイミド染料、ペリノン染料、フタロシアニン染料、トリアリルメタン系等を例示することができるが、これらの例に限定されるものではない。これらの染料は一部分散する形で存在しても良いが、マイクロカプセルを形成している殻材樹脂に溶解するものを選択することが好ましい。

【0021】本発明におけるマイクロカプセルでは、これら無彩色顔料・染料は、染料が染着した自己水分散性樹脂によって無彩色顔料が内包された着色樹脂粒子として存在する。この着色樹脂粒子（着色マイクロカプセル粒子）は分散安定性に優れており、しかも耐水性、耐光性が良好で文字の滲みがない、カラーの発色が良好である等の効果も発揮する。さらに色彩の点からも種々の有用性を示す。

【0022】例えば、異種顔料同士の着色と異なり異色の粒子の混在が少なく印刷物の色別れがなく、顔料のみでは沈みがちな発色と比べ染料の併用によって発色性の改良効果が得られる、また染料のみでは耐光性に弱いが顔料の併用によって紫外線の散乱・吸収効果によって耐光性が大幅に向上するという利点がある。更にまた、芯材の無彩色顔料がシリカやアルミナのような屈折率が小さい体質顔料の場合は、透明性が高く、染料が染着した自己水分散性樹脂によって透明で明るい発色が得られる。チタンホワイトのような屈折率が大きい白色顔料は、染料が染着した自己水分散性樹脂によって明るくかつ隠蔽性の高い発色が得られる等の利点が挙げられる。一方、芯材が黒色顔料のカーボンブラックである場合には染料による染着は調色を主たる目的にすることが出来る。特に顔料がカーボンブラックで、染料が黒色染料及び／又は青色染料である組み合わせる場合には、従来のカーボンブラックにない、高級感のある漆黒の色相の再現が可能となる。

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【0023】本発明において使用する染料と無彩色顔料の総使用量は、本発明における効果を達成すれば特に規定されないが、最終的に得られる水性インキ中で 0.5 ～ 20 重量% となるような量が好ましい。本発明における効果を達成するには、無彩色顔料に対する染料の重量比率は、1 重量% 以上 50 % 重量以下の範囲にて用いることが望ましい。

【0024】本発明における着色マイクロカプセルは、染料による樹脂の染着と同時に無彩色顔料のマイクロカプセル化を行う、染料で樹脂を染着した後に同顔料のマイクロカプセル化を行う、同顔料を内包した樹脂粒子（マイクロカプセル粒子）を染料で染着する、等の手段によって形成される。

【0025】形成された着色マイクロカプセル成分を含む本発明組成物、即ち染料が染着した自己水分散性樹脂によって無彩色顔料が内包された着色マイクロカプセルを水性媒体中に分散した本発明のインクジェット記録用組成物は、例えば合成樹脂 (I) の有機溶剤溶液に染料及び無彩色顔料を添加し、攪拌機や分散装置を用いて溶解・分散を行ってよく混合した後、塩基 (2) の存在下でそれと水性溶媒 (C) とを混合することによって調製出来る。

【0026】より具体的に説明すると、一般に転相乳化法と呼ばれるマイクロカプセル化方法によって調製することで本発明のインクジェット記録用マイクロカプセルインク組成物は容易に製造可能である。転相乳化法による製造は、基本的には第 1 段階として有機溶剤に可溶で中和によって自己水分散性を合成樹脂 (I) を有機溶剤に溶解させ、更に無彩色顔料及び染料を当該樹脂溶液中に分散、溶解させる工程（ミルベース工程）、第 2 段階としてその溶液を塩基 (2) の存在下で過剰量の水性媒体と混合させることにより、染料が染着した水分散性樹脂によって無彩色顔料を内包した樹脂粒子を得る工程（カプセル化工程）からなり、場合により、第 3 段階として、第 1 段階のミルベース工程で用いた有機溶剤を除去する工程（脱溶剤工程）を入れても良い。

【0027】前記のマイクロカプセルインク組成物の製造に際して、染料・無彩色顔料は、両方とも予め水性媒体中に分散する前の自己水分散性樹脂中に分散または溶解せしめておくことが好ましい。

【0028】また前記転相乳化法を用いてカプセル化を行う場合、第 1 段階で使用する有機溶剤はアセトン、ジメチルケトン、メチルエチルケトン等のケトン系溶剤；メタノール、エタノール、イソプロピルアルコール等のアルコール系溶剤；テトラヒドロフラン、ジオキサン等のエーテル系溶剤；クロロホルム、塩化メチレン等の塩素系溶剤；ベンゼン、トルエン等の芳香族系溶剤；酢酸エチルエステル等のエステル系溶剤；エチレングリコールモノメチルエーテル、エチレングリコールジメチルエーテル等のグリコールエーテル系溶剤；アミド類等、樹

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脂を溶解させるものであれば使用可能であるが、前記合成樹脂 (1) を用いた転相乳化法の場合、ケトン系溶剤とアルコール系溶剤から選ばれる少なくとも 1 種類以上の組み合わせが良好なマイクロカプセルを与え、この組み合わせは好適である。

【0029】本発明においては、分散剤、可塑剤、酸化防止剤、紫外線吸収剤等の添加剤を必要に応じて有機溶剤、樹脂、染料・顔料と共に用いても良い。第 2 段階のカプセル化は、上記溶剤に樹脂と染料・無彩色顔料を混合し、攪拌機や分散装置を用いて溶解・分散を行い、得られた有機溶剤溶液と水を必須成分とする水性媒体とを混合することにより行う。

【0030】第 2 段階のマイクロカプセル化では、第 1 段階で得たミルベースに塩基 (2) の存在下、水又は水溶液を混合してカプセル化を行うが、使用する無彩色顔料や染料によってはカプセル同士の緩い凝集を生ずることがあるため、カプセル化後に水又は水溶液を追加し混合分散を行うことが好ましい。この工程では、水を必須成分とする水性媒体中に、自己水分散性樹脂を含む着色溶液を加えても良いが、逆に当該樹脂を含む着色溶液中に水性媒体を加えるほうが、均一な粒子径の水性分散液が得られる点で好ましい。必要によっては界面活性剤を併用して、強制的に乳化させて得ることもできる。しかしながら界面活性剤や保護コロイドは最終的に得られる粒子の物性を低下させる傾向があるので用いないことが好まれる。

【0031】塩基 (2) はミルベースまたは水溶液に添加する。また水性媒体において用いられる水は、イオン交換水以上のグレードが好ましい。第 3 段階として、カプセル化が終了した後に第 1 段階のミルベース工程で用いた合成樹脂 (1) を溶解する有機溶剤を除去する脱溶剤工程を経ることにより、着色マイクロカプセルの膨潤・凝集を押さえ安定した水分散液が得られ、これはインクジェット記録用水性インクに適している。この脱溶剤工程において必要ならば水を除去してもよい。また勿論、この第 3 段階の工程は場合によっては省くこともある。

【0032】着色マイクロカプセル含む本発明組成物をインクジェット記録用インク組成物として実用に供するには、乾燥防止のための水溶性有機溶剤を添加剤として用いることが好ましい。乾燥防止剤としては従来知られているエチレングリコール、プロピレングリコール、ジエチレングリコール、ジプロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリン等の多価アルコール類またはそれらのアルキルエーテル類、N-メチル-2-ピロリドン、2-ピロリドン等のピロリドン類、アミド類、ジメチルスルホオキサイド、イミダゾリジノン等があり、これらに限定されるものではない。

【0033】また必要に応じて浸透性付与のための水溶性有機溶剤を加えてもよく、エタノール、イソプロピル

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アルコール等の低級アルコール、ジエチレングリコール-N-ブチルエーテル等のグリコールエーテル等を用いることができるがこれらに限定されるものではない。その他必要に応じて水溶性樹脂、pH 調整剤、分散・消泡・紙への浸透のための界面活性剤、防腐剤、キレート剤等の添加剤を加えることができる。

【0034】これらの添加剤は、第 1 段階から最終段階までの適当な工程で加えることができるが、好ましくは最終段階後の添加剤の添加は避けたほうがよい。最終の組成の調整が終了した後、フィルターを過すや遠心分離等で大粒径粒子を除去し、本発明の水性インクとすることが好ましい。

【0035】

【発明の実施の形態】本発明の好適な実施の形態を転相乳化法によって製造する場合を例にして説明すると次の通りである。

【0036】合成樹脂として、スチレン、置換スチレン、(メタ)アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、(メタ)アクリル酸とを共重して得られる、酸価が 50 以上 280 以下、分子量 1000 以上 10 万以下のビニル共重合体を有機溶媒に溶解した合成樹脂溶液と、無彩色顔料と、染料として前記合成樹脂に溶解し得る染料とを混合し練肉して着色ミルベースを得る。顔料に対する染料の重量比率は 1 重量%以上 50%重量以下の範囲とする。この着色ミルベースに前記合成樹脂の酸基を中和しうる塩基を加え、攪拌混合し、更に攪拌下に水を含む水性媒体を滴下し混合して転相乳化を行うことにより、染料が染色した自己水分散性樹脂によって無彩色顔料が内包された着色樹脂粒子が水性媒体中に分散した着色マイクロカプセルの水分散液を得る。この際、アルカリ中和剤としての塩基の添加量は、酸基の 60 モル%以上を中和する量を範囲とする。使用する無彩色顔料や染料によってカプセル同士の緩い凝集を生じた場合は、カプセル化後に水又は水溶液を追加混合して再度分散する。さらに合成樹脂の溶解に用いた有機溶媒を減圧蒸留を行って除去し、インクジェット記録用インク組成物を得る。

【0037】

【実施例】次に実施例及び比較例を挙げて本発明を更に具体的に説明する。なお、以下の実施例中における「部」は『重量部』を表わす。

【0038】(実施例 1)

カーボンブラック	20 部
スチレンアクリル酸樹脂	20 部
(スチレン/アクリル酸 2-エチルヘキシル/アクリル酸 = 77/10/13; 酸価 100、分子量 4 万)	
油性フタロシアニン染料	2 部
メチルエチルケトン	49 部
の配合物を直径 0.2 mm のガラスビーズを用いてペイントシェーカーで 4 時間練肉し、	



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メチルエチルケトン 40部  
 イソプロピルアルコール 40部  
 を加えて内容物を取り出し、ミルベース溶液171部を得た。

【0039】前記ミルベース171部にトリエタノールアミン5.3部（樹脂の中和率100%相当）を加えて攪拌しながら、グリセリン50部とイオン交換水120部の混合液を毎分5mlの速度で滴下し、着色マイクロカプセル組成物を得た。得られた着色マイクロカプセル組成物を衝突式分散装置ナノマイザー（ナノマイザー株式会社製）を用いて1500kg/cm<sup>2</sup>の圧力で再度分散処理を行った。得られた処理液にグリセリン80部とイオン交換水300部の混合液を毎分5mlの速度で滴下した後、ロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終の着色マイクロカプセル水分散物を得た。

【0040】この水分散物を1.5μmフィルターを用いてろ過を行い、インクジェット記録用マイクロカプセルインクとした。得られたインク中のマイクロカプセルは0.1μmの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を示し、インクジェットプリンターを用いた印字は安定しており、得られた印刷物は漆黒の色調を有しており、滲みもなく、耐水耐光性に優れていた。

【0041】（比較例1）実施例1のミルベースから油性フタロシアニン染料を除いた配合で同様にしてインクジェット記録用マイクロカプセルインクを得た。得られた印刷物はやや褐色を帯び、良好な色調とはいえなかった。

【0042】（実施例2）

コロイダルシリカ 2部  
 スチレンアクリル酸樹脂 40部  
 （スチレン/アクリル酸2-エチルヘキシル/アクリル酸/メタアクリル酸=72/5/10/13；酸価155、分子量4万5千）  
 油性マゼンタ染料 4部  
 メチルエチルケトン 50部  
 ガラスビーズ 150部  
 の配合物をペイントシェーカーで4時間練肉し、  
 メチルエチルケトン 40部  
 イソプロピルアルコール 40部  
 を加えて内容物を取り出し、ミルベース溶液176部を得た。

【0043】前記ミルベース176部にトリエタノールアミン16.5部（樹脂の中和率100%相当）を加えて攪拌しながら、グリセリン65部とイオン交換水210部の混合液を毎分5mlの速度で滴下し、着色マイクロカプセル組成物を得た。

【0044】得られた得られた着色マイクロカプセル液を衝突式分散装置ナノマイザー（ナノマイザー株式会

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製）を用いて1500kg/cm<sup>2</sup>の圧力で再度分散処理を行った。得られた処理液にグリセリン75部とイオン交換水210部の混合液を毎分5mlの速度で滴下した後ロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終の着色マイクロカプセル水分散物を得た。

【0045】この水分散物を1.5μmフィルターを用いてろ過を行い、インクジェット記録用マイクロカプセルインク組成物とした。得られたインク中のマイクロカプセルは0.086μmの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を示し、インクジェットプリンターを用いた印字は安定しており、得られた印刷物は明るいマゼンタ色の色調を有しており、滲みもなく、耐水耐光性に優れていた。

【0046】（比較例2）

スチレンアクリル酸樹脂 40部  
 （スチレン/アクリル酸2-エチルヘキシル/アクリル酸/メタアクリル酸=72/5/10/13；酸価155、分子量4万5千）  
 油性マゼンタ染料 4部  
 メチルエチルケトン 90部  
 イソプロピルアルコール 40部

の実施例2の配合からコロイダルシリカを除いた配合物を攪拌機で溶解し、ミルベース溶液174部を得た。

【0047】前記ミルベース174部にトリエタノールアミン16.5部（樹脂の中和率100%相当）を加えて攪拌しながら、グリセリン65部とイオン交換水210部の混合液を毎分5mlの速度で滴下し、着色樹脂乳化物を得た。

【0048】得られた得られた着色樹脂乳化物を衝突式分散装置ナノマイザー（ナノマイザー株式会社製）を用いて1500kg/cm<sup>2</sup>の圧力で再度分散処理を行った。得られた処理液にグリセリン75部とイオン交換水210部の混合液を毎分5mlの速度で滴下した後ロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終の着色樹脂乳化物を得た。この着色樹脂乳化物は5μmフィルターでもろ過が出来ず、インクジェット記録用マイクロカプセルインク組成物が得られなかった。着色樹脂乳化物は0.22μmの平均粒子径を有していたが、1μm以上の粗大粒子が約2%存在していた。

【0049】（実施例3）実施例2のスチレンアクリル樹脂に代えてスチレンアクリル酸樹脂（スチレン/アクリル酸/メタアクリル酸=65/10/25；酸価221、分子量4万5千）を用い、更に当該樹脂の中和率100%に相当する量のトリエタノールアミンを用いる以外は実施例2と同様な方法でインクジェット記録用マイクロカプセルインク組成物を調製した。得られたインク中のマイクロカプセルは0.060μmの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を

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示し、インクジェットプリンターを用いた印字は安定しており、得られた印刷物は明るいマゼンタ色の色調を有しており、滲みもなく、耐水耐光性に優れていた。

【0050】

【発明の効果】染料が染着した自己水分散性樹脂で無彩

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色顔料を内包した着色樹脂粒子が水性媒体（C）中に分散した本発明のインクジェット記録用マイクロカプセルインク組成物は、優れた発色性、耐光性を有し、また長期にわたって安定な分散を可能にする。

## PATENT ABSTRACTS OF JAPAN

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**(54) STEREOLITHOGRAPHIC RESIN AND STEREOLITHOGRAPHIC RESIN COMPOSITION**

**(57)Abstract:**

**PURPOSE:** To obtain a resin which gives a three-dimensional molding excellent in mechanical properties, thermal properties, dimensional accuracy, etc., by mixing an unsaturated urethane having a specific composition with at least one vinyl monomer in a given weight ratio.

**CONSTITUTION:** An unsaturated urethane represented by formula I (wherein X is the residue formed from a diisocyanate by removing the isocyanate groups; A1 and A2 each is a group represented by formula II or III; R1, R2, and R3 each is H or CH<sub>3</sub>; Y1 is the residue formed from a dihydric alcohol by removing the hydroxyl groups; and Y1 is the residue formed from a trihydric alcohol by removing the hydroxyl groups) is mixed with at least one vinyl monomer comprising either (meth)acrylic morpholide or a mixture thereof with a diol di(meth)acrylate (e.g. neopetyl glycol diacrylate), in a weight ratio of 100/15 to 100/150. Thus, the objective resin is obtained.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the resin for optical solid molding, and the resin constituent for optical solid molding. Although NC cutting method is carried out to manufacture of various kinds of models, such as a model for mold manufacture, a model for copying, and a model for die-sinking electric discharge machining, and a fixed form object, in recent years, the optical solid molding method which irradiates an energy line at the resin for optical solid molding which has photopolymerization nature in these manufactures, or its constituent, and carries out hardening shaping of the predetermined solid molding object attracts attention. This invention relates to the resin for optical solid molding applied to the above optical solid molding methods especially the resin for optical solid molding containing partial saturation urethane, and its constituent.

[0002]

[Description of the Prior Art] The example which contains the partial saturation urethane obtained from 1 polyurethane diisocyanate and hydroxyalkyl acrylate as resin for optical solid molding which contains partial saturation urethane conventionally (JP,2-145616,A), 2) The example containing the partial saturation urethane obtained from polyurethane diisocyanate and TORIORUJI (meta) acrylate (JP,1-204915,A, JP,63-35550,A), 3) The example containing the partial saturation urethane obtained from polyurethane diisocyanate and tetra-all thoria KURIRETO (JP,61-276863,A), 4) The example containing the partial saturation urethane obtained from poly URETANTORI - hexa isocyanate and TORIORUJI (meta) acrylate (JP,63-35550,A), 5) The example containing the partial saturation urethane obtained from tri-isocyanate, diol monochrome (meta) acrylate, or TORIORUJI (meta) acrylate (JP,63-112551,A), 6) There is an example (JP,63-20203,B) containing the partial saturation urethane obtained from diisocyanate and triol JIMETA acrylate.

[0003] However, the conventional above resin for optical solid molding and its above conventional constituent have the fault that configuration precision is bad, bad [ mechanical physical properties ] also in the physical properties of the solid molding object obtained. As a cause which worsens configuration precision of the solid molding object obtained The volume change in the process which the resin for optical solid molding or its constituent hardens, There are the heterogeneity of the ingredient in these resin or a constituent, a configuration of the solid molding object made into the purpose, etc. If uneven distortion stress occurs [ these ] inside a solid molding object conjointly and such distortion stress concentrates in the particular part and the specific direction of a solid molding object, deformation of curvature, torsion, crushing, etc. will be produced and structure destruction of a crack, exfoliation, etc. will be produced. Moreover, the solid molding object with which such distortion stress was inherent has a potentially unstable configuration, and it is easy to produce deformation with time and structure destruction by use accompanied by temperature conditions or a load etc. In the solid molding object generally obtained from the resin for optical solid molding, or its constituent, what has \*\*\*\* ductility low glass transition temperature and an elastic modulus and high tends to cause deformation, and what has \*\*\*\* ductility high glass transition temperature and low tends to produce structure destruction.

[0004] From the former, the physical properties of the solid molding object obtained and to improve especially thermal physical properties are tried. There is an example (JP,6-199962,A) which makes the both sides of an acrylate radical and a methacrylate radical contain as a polymerization nature machine for the purpose which enlarges crosslinking density of 1 solid molding object in addition to the example and the 2



[0012] (Residue Y2 excluding [ on the formula 2 and the formula 3 and ] the hydroxyl group from R1, R2, R3;H, or CH3Y1; dihydric alcohol; residue excluding the hydroxyl group from trihydric alcohol)

[0013] Vinyl monomer: (meta) Mixture of acrylic-acid mol HORIDO or (meta) acrylic-acid mol HORIDO, and JIORUJI (meta) acrylate [0014] the partial saturation urethane shown by the formula 1 — monochrome (meta) acrylate / diisocyanate [ of 1 dihydric alcohol ] = — 2/1 (mole ratio) of reactants, the reactant of di(meth)acrylate / diisocyanate 1/1/1 (mole ratio) of the monochrome (meta) acrylate / trihydric alcohol of 2 dihydric alcohol, and the reactant of di(meth)acrylate / diisocyanate =2 / 1 (mole ratio) of 3 trihydric alcohol are included.

[0015] In this invention, the monochrome (meta) acrylate of dihydric alcohol means the monoacrylate or mono-methacrylate of dihydric alcohol. Moreover, the di(meth)acrylate of trihydric alcohol means the diacrylate, dimethacrylate, or monoacrylate mono-methacrylate of trihydric alcohol.

[0016] As monochrome (meta) acrylate of dihydric alcohol, the monochrome (meta) acrylate of the dihydric alcohol of carbon numbers 2–6, such as 2-hydroxyethyl (meta) acrylate, hydroxypropyl (meta) acrylate, and 1,6-hexanediol monochrome (meta) acrylate, is mentioned.

[0017] As di(meth)acrylate of trihydric alcohol, they are a glycerol, trimethylol propane, and 5-methyl. — Although the di(meth)acrylate of trihydric alcohol, such as 1, 2, 4-heptane triol, 1 and 2, and 6-hexane triol, is mentioned, glycerin diacrylate, glycerol dimethacrylate, and glycerol monoacrylate mono-methacrylate can use it advantageously then among these.

[0018] As monochrome (meta) acrylate of dihydric alcohol and di(meth)acrylate of trihydric alcohol which were illustrated above, and diisocyanate made to react 1) Aromatic series diisocyanate, such as various kinds of tolylene diisocyanate and methylenebis - (4-phenyl isocyanate), 2) Aliphatic series diisocyanate or alicycle group diisocyanate, such as hexamethylene di-isocyanate and methylenebis (4-cyclohexyl isocyanate), 3) Aliphatic series and alicycle group diisocyanate, such as a 4-isocyanato methyl-1-isocyanato-1-methyl-cyclohexane, 5-isocyanato methyl-1-isocyanato -1, and a 1-dimethyl-5-methyl-cyclohexane (isophorone diisocyanate), are mentioned.

[0019] In the partial saturation urethane shown by the formula 1, when using the di(meth)acrylate of two sorts of trihydric alcohol which is different when using the monochrome (meta) acrylate of two sorts of different dihydric alcohol, and when using the monochrome (meta) acrylate of dihydric alcohol, and the di(meth)acrylate of trihydric alcohol, each partial saturation urethane obtained turns into unsymmetrical form partial saturation urethane. As diisocyanate used for compounding this unsymmetrical form partial saturation urethane What has an isocyanate radical which is influenced of the substituent of steric hindrance nature, and an isocyanate radical which is not influenced [ the ], Or the thing which has the isocyanate radical combined with the isocyanate radical combined with the aliphatic hydrocarbon radical, and the aromatic hydrocarbon radical, It is desirable to use mutually the diisocyanate which has the isocyanate radical from which a reactant radical differs. As this diisocyanate 2, 4-tolylene diisocyanate, isophorone diisocyanate, a 4-isocyanato methyl-1-isocyanato-1-methyl-cyclohexane, etc. are mentioned.

[0020] Although especially this invention does not restrict the synthetic approach of partial saturation urethane and can apply a well-known approach, for example, an approach which is indicated by JP,4-53809,A, to the composition In composition of unsymmetrical form partial saturation urethane Make one mol of diisocyanate which has the isocyanate radical on which the above mentioned reactivity differs from the monochrome (meta) acrylate of dihydric alcohol, or one mol of di(meth)acrylate of trihydric alcohol beforehand react, and it considers as partial saturation urethane

mono-isocyanate. Subsequently, the approach to which the monochrome (meta) acrylate of different dihydric alcohol from the above or the di(meth)acrylate of trihydric alcohol is made to react is desirable.

[0021] According to this invention, in the partial saturation urethane shown by the formula 1, what has 3 or four polymerization nature machines in a molecule is desirable, and what has the both sides of an acryloyl radical and a methacryloyl radical as a polymerization nature machine is still more desirable. In this case, although especially the rate of the acryloyl radical as a polymerization nature machine and methacryloyl radical which are contained in a molecule is not restricted, it is desirable to consider as the ratio of an acryloyl radical / methacryloyl radical = 2/1, when the number of polymerization nature machines is three, and to consider as the ratio of an acryloyl radical / methacryloyl radical = 2 / 2 - 3/1, when the number of polymerization nature machines is four.

[0022] The resin for optical solid molding of this invention consists of the partial saturation urethane and the vinyl monomer which are shown by the formula 1, and this vinyl monomer consists of the independent system of acrylic-acid (meta) mol HORIDO, or (meta) the mixed stock of acrylic-acid mol HORIDO and JIORUJI (meta) acrylate.

[0023] (Meta) As acrylic-acid mol HORIDO, although acrylic-acid mol HORIDO and methacrylic-acid mol HORIDO are mentioned, acrylic-acid mol HORIDO is desirable.

[0024] (Meta) As JIORUJI (meta) acrylate in the case of mixing with acrylic-acid mol HORIDO and using 1) Ethylene glycol, propylene glycol, 1,4-butanediol, Diacrylate or dimethacrylate of alkane diol of carbon numbers 2-6, such as neopentyl glycol and 1,6-hexanediol, 2) Cyclohexane dimethanol, cyclohexene dimethanol, JISHIKURO pentyl dimethanol, etc., Diacrylate or dimethacrylate of the diols which have the alicyclic hydrocarbon radical of carbon numbers 6-12, 3) Make the aliphatic series lactone or aliphatic series hydroxy acid of carbon numbers 4-6 react to the above mentioned alkane diol and diols, and are obtained. Diacrylate or dimethacrylate of a 1,6-hexanediol hydronalium KISHIKA plate, Diacrylate or dimethacrylate of the neopentyl glycol hydroxy pivalate etc., Diacrylate or dimethacrylate of ester diol, (Pori) 4) 2 and 2-screw (hydroxy ethoxy phenyl) propane, 2, and 2-screw (hydroxy diethoxy phenyl) propane, Diacrylate or dimethacrylate of alkoxy \*\* bisphenols of an alkoxyl group, such as screw (hydroxy propoxy phenyl) methane and screw (hydroxy dipropoxy phenyl) methane, etc. is mentioned. [ of carbon numbers 2-3 ]

[0025] In this invention, when using the mixed stock of acrylic-acid mol HORIDO and JIORUJI (meta) acrylate as a vinyl monomer (meta), as for acrylic-acid (meta) mol HORIDO, it is desirable to make it contain at 50% of the weight or more of a rate in a vinyl monomer, and it is still more desirable to make it contain at 60% of the weight or more of a rate.

[0026] the resin for optical solid molding of this invention — setting — the rate of partial saturation urethane and a vinyl monomer — this partial saturation urethane/— this — it is vinyl monomer = 100 / 25 - 100/150 (weight ratio), and is 100 / 40 - 100/100 (weight ratio) preferably.

[0027] The resin constituent for optical solid molding of this invention makes resin for optical solid molding which was explained above contain one sort of the filler chosen from a solid-state particle with a mean particle diameter of 0.1-50 micrometers and the inorganic fiber whisker of 1-70 micrometers of mean fiber length, or two sorts or more. When using an inorganic fiber whisker as a filler, a thing 10 micrometers or more has [ the diameter of fiber ] mean fiber length desirable [ when using a solid-state particle as a filler, a thing 3 micrometers or more has desirable mean particle diameter, and ] at 0.3-1 micrometer. As this filler, inorganic fiber whiskers, such as organic solid-state particles, such as inorganic solid-state particles, such as one silica, an alumina, clay, a calcium carbonate, and a glass bead, 2 bridge-formation polystyrene, polymethylmethacrylate, and the poly methyl siloxane, 3 potassium titanate fibers,



magnesium sulfate fiber, boric-acid magnesium fiber, boric-acid aluminum fiber, and a carbon fiber, are mentioned. the case where these fillers are made to contain — per [ said / which was carried out ] resin 100 weight section for optical solid molding — a filler — the 50 – 400 weight section — comparatively — becoming — making .

Although these fillers can use one sort or two sorts or more, it is desirable to use the both sides of an inorganic solid-state particle and an inorganic fiber whisker as a filler, and it is still more desirable to use the 50 – 300 weight section and an inorganic fiber whisker for an inorganic solid-state particle at a rate of the 10 – 100 weight section in this case.

[0028] When presenting optical solid molding with the resin for optical solid molding of this invention, and its constituent, these are made to contain a photopolymerization initiator beforehand. Although this invention does not restrict especially the class of photopolymerization initiator to be used, as this photopolymerization initiator, polynuclear aromatic compounds, such as sulfur compounds, such as carbonyl compounds, such as one benzoin, alpha-methyl benzoin, anthraquinone, KURORU anthraquinone, and an acetophenone, 2 diphenyl sulfide, diphenyl disulfide, and dithiocarbamate, a 3alpha-KURORU methylnaphthalene, and an anthracene, etc. are mentioned. It is made for the content of the photopolymerization initiator in the resin for optical solid molding and its constituent to usually serve as 0.1 – 10 weight section, and is made to serve as 1 – 5 weight section preferably per resin 100 weight section for optical solid molding. With a photopolymerization initiator, photosensitizers, such as n butylamine, triethanolamine, N, and N-dimethylamino benzenesulfonic acid diaryl amide, N, and N-dimethylaminoethyl methacrylate, can be used.

[0029] This invention does not restrict especially the optical solid molding method that applies the resin for optical solid molding of this invention, or its constituent. Various kinds of approaches are learned as this optical solid molding method (JP,56-144478,A, JP,60-247515,A, JP,1-204915,A, JP,3-41126,A, etc.). To this for example The hardening layer of the resin for optical solid molding or its constituent is made to form first, and next, the resin for optical solid molding or its constituent is newly supplied on this hardening layer, it carries out by repeating actuation of making the hardening layer form, and there is a method of making a desired solid molding object form. Postcure of this solid molding object can also be carried out further if needed. As an energy line used for hardening, although a visible ray, ultraviolet rays, an electron ray, etc. are mentioned, ultraviolet rays are desirable.

[0030] Although an example and the example of a comparison are given and the configuration and effectiveness of this invention are hereafter made more concrete, it is not that this invention is limited to this example. In addition, in the following examples and examples of a comparison, unless it uses in another semantics especially, the section means the weight section and % means weight %.

[0031]

[Example]

Test partition 1 (preparation of the resin for optical solid molding)

– According to the synthesis method indicated by examples 1–8 and the example 1 of a comparison – 5 JP,4-53809,A, partial saturation urethane A-1 (thing to which glycerol monoacrylate mono-methacrylate, hydroxyethyl acrylate, and 2 and 4-tolylene diisocyanate were made to react by the mole ratio of 1/1/1) was compounded. The mixed dissolution of the 67 sections was carried out [ compound partial saturation urethane A-1 ] for the 100 sections and acrylic-acid mol HORIDO at the room temperature, and the resin for optical solid molding of an example 1 was prepared. The resin for optical solid molding of examples 2–8 and the examples 1–5 of a comparison was prepared like the example 1. These presentations were collectively shown in Table 1.

[0032]

[Table 1]

区 分	不飽和ウレタン		ビニル単量体	
	種 類	使用量(部)	種 類	使用量(部)
実施例 1	A-1	100	B-1	67
2	A-2	100	B-1	67
3	A-3	100	B-1	67
4	A-1	100	B-1/C-1	47/20
5	A-2	100	B-1/C-2	47/20
6	A-3	100	B-1/C-3	47/20
7	A-2	100	B-2	122
8	A-3	100	B-2	33
比較例 1	A-1	100	C-1	67
2	A-2	100	C-2	67
3	A-3	100	C-3	67
4	A-1	100	B-1/C-1	200/100
5	A-2	100	B-1/C-2	7/3

[0033] In Table 1 A-1 : Glycerol monoacrylate mono-methacrylate / hydroxyethyl acrylate / 2, the reactant A-2:glycerin diacrylate / hydroxyethyl methacrylate / 2 of 4-tolylene diisocyanate =1/1/1 (mole ratio), 4-tolylene diisocyanate =1/1/1 Reactant A-of (mole ratio) 3 : Reactant B-1:acrylic-acid mol HORIDO B-2 of hydroxyethyl methacrylate / hydroxyethyl acrylate / isophorone diisocyanate =1/1/1 (mole ratio) : Methacrylic-acid mol HORIDO C-1:neopentyl-glycol-diacrylate C-2 : JISHIKURO pentyl dimethylene diacrylate C-3: Neopentyl glycol hydroxy pivalate diacrylate [0034] Test partition 2 (production and its evaluation of a solid molding object)

1) The optical solid molding equipment which main-consisted of a three-dimensions NC table equipped with the production container of a solid molding object and a helium cadmium laser light (output [ of 25mW ], wavelength of 3250A) control system was used. What dissolved the 1-hydroxy cyclohexyl phenyl ketone 3 section in the above-mentioned container as a photopolymerization catalyst per [ which was prepared in the test partition 1 ] resin 100 section for optical solid molding It is filled up with (this is only hereafter called mixed liquor), and this mixed liquor is supplied to a horizontal plane (X-Y-axis flat surface) by the thickness of 0.10mm from this container. The helium cadmium laser light which converged from the perpendicular direction (Z shaft orientations) to the front face (X-Y-axis flat surface) was scanned, and the resin for optical solid molding was stiffened. Next, mixed liquor was newly supplied by the thickness of 0.10mm on this hardened material, and it was made to harden similarly. Hereafter, similarly, the laminating of a total of 200 layers was carried out, and the design value molded the stereo of the diameter of 200.00mm at the bottom, and a cone configuration with a height of 20.00mm. After washing the obtained molding object by isopropyl alcohol, it irradiated for 30 minutes with the ultraviolet ray lamp of 3Kw, the post cure was performed, and the solid molding object was obtained.

[0035] 2) It is JIS like the measurement 1 of mechanical physical properties. After carrying out the Mitsuzo form of the bumb bell shape with a thickness of 3mm set to K7113 and washing the molding object by isopropyl alcohol, it heated at 98 degrees C for 2 hours, the post cure was performed, and the test piece was produced. A test piece produces the three same things and is JIS. According to K7113, it is 5mm/second in speed of testing, and tensile strength, a modulus of elasticity in tension, and \*\*\*\* ductility were measured. Moreover, the toughness value (Tf) shown with tensile strength x \*\*\*\* ductility was computed. The result was shown in Table 2

as the average of three test pieces.

[0036] 3) The test piece of a 55mmx10mmx2mm monotonous form as well as the test piece of the measurement 2 of thermal physical properties was produced. Dynamic viscoelasticity was measured about this test piece, and it asked for the glass transition temperature (T<sub>g</sub>) shown by T<sub>delta</sub>. The result was shown in Table 2.

[0037] 4) About the solid molding object obtained by the measurement 1 of a configuration, perpendicular projection of the two-dimensional graphic form a was carried out at X-Y-axis flat surface, and level projection of the two-dimensional graphic form b was carried out to 50 arbitrary flat surfaces perpendicular to X-Y-axis flat surface, and measurement shown below about such projection drawing was performed. The result was shown in Table 3. In addition, the two-dimensional graphic form a acquired here is circular, and the two-dimensional graphic form b is a triangle. Two-dimensional graphic form a: 50 straight lines of the arbitration passing through the center of gravity of projection drawing were pulled, the distance for two points which crosses the profile of this projection drawing was measured, and the average, maximum, the minimum value, and standard deviation were computed about such measured value.

The area of the projection drawing of b:50 two-dimensional graphic forms was measured, and the average, maximum, the minimum value, and standard deviation were computed about such measured value.

[0038]

[Table 2]

区 分	機 械 的 物 性				熱的物性
	引張強度 Kgf/mm <sup>2</sup>	引張彈性率 Kgf/mm <sup>2</sup>	引張伸度 %	T f Kgf/mm <sup>2</sup>	T g ℃
実施例 1	12.9	410	5.6	72	198
2	13.0	422	5.0	65	197
3	10.8	368	6.7	72	154
4	12.9	404	4.9	63	192
5	12.4	387	4.7	58	193
6	10.2	315	6.2	63	137
7	13.5	433	4.4	59	211
8	11.6	370	5.0	58	165
比較例 1	9.5	348	1.7	16	134
2	9.4	316	1.8	17	130
3	8.0	238	2.9	23	123
4	8.4	259	2.2	18	139
5	14.0	430	1.1	15	206
6	4.1	250	11.5	47	110

[0039]

[Table 3]

区 分	形 状							
	2 次 元 図 形 a				2 次 元 図 形 b			
	平均値 mm	最大値 mm	最小値 mm	標準偏差 mm	平均値 mm <sup>2</sup>	最大値 mm <sup>2</sup>	最小値 mm <sup>2</sup>	標準偏差 mm <sup>2</sup>
実施例 1	199.04	199.24	198.83	0.10	1984	1988	1980	1.9
2	199.03	199.25	198.82	0.11	1983	1987	1979	1.9
3	199.17	199.34	198.99	0.09	1987	1991	1982	2.0
4	198.88	199.25	198.50	0.18	1982	1989	1974	3.1
5	198.84	199.18	198.56	0.16	1981	1987	1974	3.0
6	199.12	199.40	198.84	0.14	1985	1992	1978	3.3
7	198.61	199.07	198.15	0.21	1979	1989	1970	4.7
8	199.22	199.60	198.81	0.20	1987	1996	1979	4.1
比較例 1	197.87	198.82	196.80	0.50	1970	1995	1949	11.4
2	197.19	199.01	197.10	0.45	1973	1994	1950	10.2
3	198.51	199.37	197.64	0.34	1977	1996	1957	9.6
4	198.37	199.18	197.53	0.41	1976	1987	1954	10.3
5	198.24	199.98	197.47	0.35	1974	1992	1957	8.1
6	—	—	—	—	—	—	—	—

[0040] It sets to Table 2 and 3, and they are example of comparison 6:ABS plastics (diamond pet HF-5 by the Mitsubishi rayon company).

In addition, injection molding of the test piece for mechanical physical-properties measurement of the example 6 of a comparison and the test piece for thermal physical-properties measurement was carried out with the cylinder temperature of 200 degrees C, and the mold temperature of 60 degrees C. The dimension and configuration of an injection-molding object are the same as said 2 and 3 respectively.

[0041] Test partition 3 (preparation of the resin constituent for optical solid molding) – The resin 100 section for optical solid molding of examples 9–12 and the example 7 of a comparison, and the example 1 prepared in 8 test partitions 1, the photopolymerization initiator 3 section, the inorganic solid-state particle 200 section, and the inorganic fiber whisker 50 section were supplied to the mixing chamber equipped with the biaxial stirrer, and churning mixing was fully carried out until it became uniform. The churning mixture was filtered through 50-micrometer filter, and the resin constituent for optical solid molding of an example 9 was prepared. The resin constituent for optical solid molding of examples 10–12 and the examples 7 and 8 of a comparison was prepared like the example 9. These presentations were collectively shown in Table 4.

[0042] Test partition 4 (production and its evaluation of a solid molding object)

1) The design value molded the stereo of the diameter of 200.00mm at the bottom, and a cone configuration with a height of 20.00mm like production of the solid molding object of the test partition 2 using the resin constituent for optical solid molding prepared in the production test partition 3 of a solid molding object. After washing the obtained molding object by isopropyl alcohol, it heated at 98 degrees C for 2 hours, the post cure was performed, and the solid molding object was obtained.

[0043] 2) Measurement of mechanical physical properties, thermal physical properties, and a configuration was performed about the solid molding object produced by the test piece produced independently and 1 like the measurement test partition 2 of mechanical physical properties, thermal physical properties, and a configuration. The result was shown in Table 5 and 6.

[0044]

[Table 4]

区 分	光学的立体造形用樹脂		無機繊維ウイスキー		無機固体微粒子		光重合開始剤	
	種 類	使用量 (部)	種 類	使用量 (部)	種 類	使用量 (部)	種 類	使用量 (部)
実施例 9	実施例 1	100	D-1	50	E-1	200	F-1	3
10	実施例 3	100	D-1	50	E-1	200	F-1	3
11	実施例 5	100	D-1	50	E-1	200	F-1	3
12	実施例 7	100	D-1	40	E-2	150	F-1	3
比較例 7	比較例 1	100	D-1	50	E-1	200	F-1	3
8	比較例 3	100	D-1	50	E-1	200	F-1	3

[0045] It sets to Table 4 and is the boric-acid aluminum whisker (Shikoku formation shrine Alvo REXX YS- 4) of 20 micrometers of D-1: pitch-diameter [ of 0.8 micrometers ] x mean fiber length.

E-1: The glass bead of 30 micrometers of mean diameters (GB-730C made from Toshiba BARODINI)

E-2: An aluminum hydroxide with a mean particle diameter of 8 micrometers (B-103 by Nippon Light Metal Co., Ltd.)

F-1: 1-hydroxy cyclohexyl phenyl ketone [0046]

[Table 5]

区 分	機 械 的 物 性				熱的物性
	引張強度 Kgf/mm <sup>2</sup>	引張弾性率 Kgf/mm <sup>2</sup>	引張伸度 %	T f Kgf/mm <sup>2</sup>	T g ℃
実施例 9	11.4	1360	1.6	18	203
10	9.6	1210	2.0	19	157
11	11.0	1290	1.6	18	195
12	11.8	1330	1.5	18	214
比較例 7	8.6	1290	0.9	7.7	139
8	7.4	1010	1.1	8.1	127

[0047]

[Table 6]

区 分	形 状							
	2 次 元 図 形 a				2 次 元 図 形 b			
	平均値 mm	最大値 mm	最小値 mm	標準偏差 mm	平均値 mm <sup>2</sup>	最大値 mm <sup>2</sup>	最小値 mm <sup>2</sup>	標準偏差 mm <sup>2</sup>
実施例 9	199.54	199.63	199.45	0.04	1993	1996	1991	1.0
10	199.63	199.82	199.55	0.04	1994	1997	1990	1.2
11	199.50	199.67	199.42	0.08	1993	1996	1989	1.7
12	199.51	199.73	199.30	0.10	1993	1998	1988	2.1
比較例 7	199.19	199.75	198.56	0.27	1987	1996	1977	4.5
8	199.30	199.82	198.77	0.24	1988	1997	1979	4.2

[0048] [0049] the crack was accepted to be to the front face of the example 7 of a comparison, and a 8:solid molding object in Table 5 and 6

[Effect of the Invention] There is already effectiveness that the solid molding object which was excellent in mechanical physical properties and thermal physical properties,

and was excellent in configuration precision can be obtained in this invention explained above so that clearly.

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(54) 【発明の名称】 インクジェット記録用水性インク及びその製造方法

(57) 【要約】

【解決手段】 酸価が 50 以上 280 以下で、酸基の 60 モル% 以上がアルカリ性の中和剤により中和されている自己水分散性樹脂に内包された着色剤からなる着色樹脂粒子 (染料粒子) が分散したインクジェット記録用水性インク。

【効果】 本発明のインクジェット記録用水性インクは、印刷品質・耐水性・耐光性に優れた樹脂分散型インクの特長を殺すことなく、分散安定性に優れ、かつノズル目詰まりもなく、安定したインクジェット噴射特性を可能にする。

(2)

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## 【特許請求の範囲】

【請求項1】 酸価が50以上280以下の合成樹脂

(a)の少なくとも一部の酸基が塩基(b)で中和されてなる自己水分散性樹脂(A)によって着色剤(B)が内包された着色樹脂粒子が、水を必須成分とする水性媒体中に分散していることを特徴とするインクジェット記録用水性インク。

【請求項2】 合成樹脂(a)が、ガラス転移温度50℃以上の樹脂である請求項1記載のインクジェット記録用水性インク。

【請求項3】 合成樹脂(a)の酸基の60モル%以上が塩基(b)で中和されている自己水分散性樹脂(A)である請求項1記載のインクジェット記録用水性インク。

【請求項4】 合成樹脂(a)が、スチレン、置換スチレン、(メタ)アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、(メタ)アクリル酸との共重合体である請求項1又は2記載のインクジェット記録用水性インク。

【請求項5】 合成樹脂(a)の必須モノマー成分が、スチレンモノマー、アクリル酸モノマー、メタアクリル酸モノマーである請求項4記載のインクジェット記録用水性インク。

【請求項6】 合成樹脂(a)の必須モノマー成分構成比率がスチレンモノマー60～90モル%、アクリル酸モノマー5～15モル%、メタアクリル酸モノマー5～25モル%である請求項5記載のインクジェット記録用水性インク。

【請求項7】 塩基(b)が、アルコールアミンである請求項1、2又は3記載のインクジェット記録用水性インク。

【請求項8】 さらに乾燥防止剤としての水溶性有機溶媒を含有する請求項1記載のインクジェット記録用水性インク。

【請求項9】 乾燥防止剤としての水溶性有機溶媒がグリセリンである請求項8記載のインクジェット記録用水性インク。

【請求項10】 酸価が50以上280以下の合成樹脂(a)の少なくとも一部の酸基が塩基(b)で中和された自己水分散性樹脂(A)の有機溶剤溶液に着色剤

(B)が分散又は溶解した着色樹脂溶液と、水を必須成分とする水性媒体(C)とを混合して転相乳化を行い、着色剤(B)を該樹脂(A)で内包させた着色樹脂粒子を水性媒体(C)中に分散させ、次いで、得られた水性分散液から前記有機溶媒を除去することを特徴とするインクジェット記録用水性インクの製造方法。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明はインクジェット記録用水性インクに関し、詳しくは、着色剤を含有する自己水分

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散性樹脂が水性媒体中に分散されたインクジェット記録用水性インクに関する。

【0002】

【従来の技術】インクジェット記録用インクは大別すると油性インクと水性インクがあるが、油性インクは臭気・毒性の点で問題があり、水性インクが主流となりつつある。

【0003】しかしながら、従来の水性インクの多くは着色剤として水溶性染料を用いているため耐水性や耐光性が悪いという欠点を有していた。また、染料が分子レベルで溶解しているため、オフィスで一般に使用されているコピー用紙などのいわゆる普通紙に印刷すると髭状のフェザリングと呼ばれるブリードを生じて著しい印刷品質の低下を招いていた。

【0004】上記欠点を改良するためにいわゆる水性の顔料インクが過去に様々に提案されており、例えばバインダー兼分散剤として水溶性樹脂を用いてカーボンブラックや有機顔料を分散させた樹脂溶解型のインクやポリマーラテックスあるいはマイクロカプセルとして着色剤を内包する樹脂分散型のインクが各種提案されている。

【0005】樹脂溶解型の水性インクは、インクの水分蒸発に伴いノズル付近のインク粘度上昇による異常噴射や、最悪ノズル目詰まりを生じ易かった。また、水溶性樹脂を用いているために耐水性が十分とはいえなかった。

【0006】樹脂分散型の水性インクは、インクの水分蒸発に伴う粘度上昇は比較的少なく、また耐水性に優れるという利点がある。具体的には、特開昭58-45272号公報では染料を含有したウレタンポリマーラテックスを含むインク組成物、特開昭62-95366号公報では水不溶性有機溶媒中にポリマーと油性染料を溶解し、さらに表面活性剤を含む水溶液と混合して乳化させた後に溶媒を蒸発してポリマー粒子中に内包された染料を含むインクが提案され、特開昭62-254833号公報ではカプセル化時の有機溶媒と水との間の界面張力を10ダイン以下にすることによる着色料水性懸濁液の製造法が提案され、特開平1-170672号公報では同様にマイクロカプセル化した色素を含有する記録液等が提案されているが、それらで得られた着色樹脂分散物の分散安定性は必ずしも十分ではなく、またカプセル化時に使用する表面活性剤の影響で泡立ちが大きく、インクジェットの噴射特性が必ずしも十分ではなかった。また、特開平3-221137号公報では、一般的な微小カプセルおよびその製造方法ならびにその用途がとして、0.1μm以下の水準に自己分散する自己分散性樹脂を用いて微小カプセルを形成する方法が提案されているが、0.1μm以下の水準に自己分散する樹脂に限定されるために使用できる樹脂が少なく、また得られるマイクロカプセルのインクジェット特性は必ずしも十分ではなかった。

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【0007】

【発明が解決しようとする課題】本発明が解決しようとする課題は、印刷品質・耐水性・耐光性に優れた樹脂分散型水性インクの特長を殺すことなく、分散安定性に優れ、かつノズル目詰まりもなく、安定したインクジェット噴射特性を有する、着色剤が自己水分散性樹脂によって内包された着色樹脂粒子が水性媒体中に分散した、インクジェット記録用水性インクを提供することにある。

【0008】

【課題を解決するための手段】本発明者等は、上記の課題を解決するために鋭意研究を重ねた結果、本発明を解決するに至った。

【0009】即ち、本発明は、酸価が50以上280以下の合成樹脂(a)の少なくとも一部の酸基が塩基

(b)、好ましくはアルコールアミンで中和されてなる自己水分散性樹脂(A)によって着色剤(B)が内包された着色樹脂粒子が、水を必須成分とする水性媒体

(C)、好ましくは乾燥防止剤としての水溶性有機溶媒を含有する水性媒体中に分散していることを特徴とするインクジェット記録用水性インクを提供する。

【0010】また、本発明は、酸価が50以上280以下の合成樹脂(a)の少なくとも一部の酸基が塩基

(b)で中和された自己水分散性樹脂(A)の有機溶剤溶液に着色剤(B)が分散又は溶解した着色樹脂溶液と、水を必須成分とする水性媒体(C)とを混合して転相乳化を行い、着色剤(B)を該樹脂(A)で内包させた着色樹脂粒子を水性媒体(C)中に分散させ、次いで、得られた水性分散液から前記有機溶媒を除去することを特徴とするインクジェット記録用水性インクの製造方法を提供する。

【0011】本発明のインクジェット記録用水性インクは、着色剤(B)を水分散性樹脂(A)で内包させた着色樹脂粒子からなる着色マイクロカプセルが水を必須成分とする水性媒体中に分散したものである。

【0012】かかる水分散性樹脂(A)は、その酸価が50以上280以下の合成樹脂(a)で、その少なくとも一部の酸基が塩基(b)、即ちアルカリ性の中和剤によって中和されたものである。

【0013】合成樹脂(a)の酸価が50未満の時は、得られた着色剤粒子の水分散安定性が十分ではなく、また酸価が280を越える場合には有機溶媒に溶解した水分散性樹脂の塩基による中和の際に凝集を生じ易く、また水に添加した際に一部の樹脂が溶解することによってノズル目詰まりを生じ易いことから、インクジェット記録用としては水分散性の樹脂の酸価は、50以上280以下の範囲で、好ましくは70~250の範囲である。

【0014】合成樹脂(a)の酸基としては、例えばカルボン酸基、スルホン酸基、スルフィン酸基等であって特に限定されるものではないが、このうちカルボキシル基は一般的であり、良好な自己水分散性樹脂を与える。

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【0015】またこの合成樹脂(a)のガラス転移温度としては、50℃未満であっても記録紙への印刷後の文字の定着性は良好であるが、ノズル目詰まりや貯蔵安定性を更に高めることを考慮するとガラス転移温度が好ましくは50℃以上、より好ましくは60℃以上のものがインクジェット記録用として好適である。

【0016】このような合成樹脂(a)としては、上記特性を満足していればどれでも良いが、スチレンあるいは $\alpha$ -メチルスチレンのような置換スチレン、アクリル酸メチルエステル、アクリル酸エチルエステル、アクリル酸ブチルエステル、アクリル酸2-エチルヘキシルエステル等のアクリル酸エステル、メタクリル酸メチルエステル、メタクリル酸エチルエステル、メタクリル酸ブチルエステル、メタクリル酸2-エチルヘキシル等のメタクリル酸エステルから選ばれる少なくとも一つ以上のモノマー単位と、アクリル酸、メタクリル酸から選ばれる少なくとも一つ以上のモノマー単位を含む共重合体が好ましく、さらに好ましくは自己水分散性樹脂(A)の必須モノマー成分としてスチレンモノマー、アクリル酸モノマー、メタアクリル酸モノマーを用いてなる共重合体であり、特にこれら必須モノマー成分の構成比率がスチレンモノマー60~90モル%、アクリル酸モノマー5~15モル%、メタアクリル酸モノマー5~25モル%である場合にはインクジェット記録用としてノズル目詰まりのない優れた着色樹脂粒子を可能とする。

【0017】前記樹脂(a)の分子量範囲についても特に制限はないが1000以上10万以下の分子量のものがより好ましい。勿論、かかる樹脂から得られた自己水分散性樹脂が水性媒体との組み合わせで安定な着色樹脂粒子を形成するものであれば、これらに特に限定されるものではなく、同時に2種類以上を混合して使用しても良い。

【0018】前記した合成樹脂(a)の酸基を塩基

(b)によって中和する、即ちアルカリ性中和剤による中和は、水分散性樹脂が水に溶解しない程度に中和する必要があり、溶解しない程度であればアルカリ性中和剤を過剰に加えても良いが、合成樹脂(a)の酸基の60モル%以上を中和するのが好ましい。中和率が60モル%以上であると、得られる着色樹脂粒子は微粒でかつ分散安定性に優れている。

【0019】自己水分散性樹脂(A)の使用量は、本発明における効果を達成すれば特に規定されないが、最終的に得られる水性インキ中で0.5~20重量%となるような量が好ましい。

【0020】塩基(b)(アルカリ性中和剤)としては、例えば水酸化ナトリウム、水酸化カリウム、水酸化リチウム等のアルカリ金属の水酸化物、アンモニア、トリエチルアミン、モルホリン等の塩基性物質の他、トリエタノールアミン、ジエタノールアミン、N-メチルジエタノールアミン等のアルコールアミンが使用可能であ

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り、特にアルコールアミンの使用が好ましい。アルコールアミンであると、より着色樹脂粒子(B)の分散安定性に優れ、また水分や有機溶剤の蒸発に伴う粒子凝集によるノズル目詰まりが改良されたインクジェット記録用インクが得られる。

【0021】本発明で使用される酸基を有する合成樹脂(a)にかかる塩基(b)を添加して中和する方法としては、予め該樹脂の有機溶媒溶液に添加するか、該樹脂の有機溶媒溶液と水媒体とを混合する際に水媒体中に添加するか等の方法があるが、その採用については最も良い条件を選択すればよい。

【0022】本発明での着色剤は、カーボンブラック、チタンブラック、チタンホワイト、硫化亜鉛、ベンガラ等の無機顔料やフタロシアニン顔料、モノアゾ系、ジスアゾ系等のアゾ顔料、フタロシアニン顔料、キナクリドン顔料等の有機顔料のほか、モノアゾ系、ジスアゾ系、金属錯塩系、アントラキノン系、トリアリルメタン系等の油性染料や分散染料等の染料が用いられるが、これらに限定されるものではない。これら着色剤の添加にあたっては、そのままでも溶液又は分散液の形態でもよい。これらの着色剤はマイクロカプセルを形成している樹脂の中に分散又は溶解する形で存在する。かかる着色剤の使用量は、本発明における効果を達成すれば特に規定されないが、最終的に得られる水性インク中で0.5~20重量%となるような量が好ましい。

【0023】本発明の自己水分散性樹脂としては、特開平3-221137号公報のような平均粒径が0.1μm以下の水準に自己分散する分散能を有する自己水分散性樹脂類を用いる必要はない。また、微小なマイクロカプセルを形成するために、本発明の水性インクには必ずしも界面活性剤の併用は必要としない。

【0024】本発明では、着色剤は水性媒体中に分散される前に予め自己水分散性樹脂を含む有機溶剤溶液中に分散または溶解せしめられるのが好ましい。即ち、有機溶媒の存在下に合成樹脂(a)、塩基(b)及び着色剤(B)を攪拌機や分散装置を用いてよく混合して、着色剤の溶解又は分散と合成樹脂の自己水分散化とを行った後、当該着色樹脂溶液と水性媒体とを混合することによって着色剤を含む自己水分散性樹脂溶液の小滴が水性媒体中に分散される。

【0025】本発明において好適な製造方法としては、一般にはミルベースと呼ばれる合成樹脂(a)を含む有機溶剤溶液中に、着色剤を分散又は溶解せしめておき、この着色ミルベースに更に塩基を混合溶解し、中和して自己分散性樹脂とし(第1段階)、その後、滴下等で水を必須成分とする水性媒体と混合して乳化させる、即ち転相乳化を行なう(第2段階)のがよい。この場合、水を必須成分とする水性媒体中に、自己水分散性樹脂を含む着色溶液を加えても良いが、逆に当該樹脂を含む着色溶液中に水性媒体を加えるほうが、均一な粒子径の水性

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分散液が得られる点で好ましい。必要によっては界面活性剤を併用して、強制的に乳化させて得ることもできる。しかしながら界面活性剤や保護コロイドは最終的に得られる粒子の物性を低下させる傾向があるので用いないことが好まれる。転相乳化法によれば、着色剤(B)が樹脂(A)に内包され、一体化した粒子が水性媒体中に分散されるので好ましい。

【0026】樹脂を溶解する際に用いられる有機溶媒としては、例えばアセトン、ジメチルケトン、メチルエチルケトン等のケトン系溶媒、メタノール、エタノール、イソプロピルアルコール等のアルコール系溶媒、クロロホルム、塩化メチレン等の塩素系溶媒、ベンゼン、トルエン等の芳香族系溶媒、酢酸エチルエステル等のエステル系溶媒、エチレングリコールモノメチルエーテル、エチレングリコールジメチルエーテル等のグリコールエーテル系溶媒、アミド類等樹脂を溶解させるものであれば使用可能であるが、樹脂成分がアクリル系樹脂の場合にはケトン系溶媒とアルコール系溶媒から選ばれる少なくとも1種類以上の組み合わせが良い。かかる有機溶媒の使用量は、本発明における効果を達成すれば特に規定されないが、合成樹脂/該有機溶媒の重量比が1/1~1/20となるような量が好ましい。

【0027】上記合成樹脂溶液には、添加剤として、必要に応じて分散剤、可塑剤、酸化防止剤、紫外線吸収剤等を溶媒、樹脂、着色剤と共に用いても良い。上記着色樹脂溶液と混合される、水性媒体において用いる水は、主としてジェットインクとして用いるため、ノズル目詰まりを回避するためにイオン交換水以上のグレードの水が好ましい。またインクジェット記録用インクが乾燥するのを防止するためには、水溶性有機溶媒を乾燥防止剤として当該インク中に存在させておくのが好ましい。当該乾燥防止剤は、転相乳化時にあるいは乳化後に、水性媒体中に添加すれば良い。かかる乾燥防止剤としては、インクジェットの噴射ノズル口でのインクの乾燥を防止する効果を与えるものであり、通常水の沸点以上の沸点を有するものが使用される。このような乾燥防止剤としては、従来知られているエチレングリコール、プロピレングリコール、ジエチレングリコール、ジプロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリン等の多価アルコール類またはそれらのアルキルエーテル類、N-メチル-2-ピロリドン、2-ピロリドン等のピロリドン類、アミド類、ジメチルスルホオキシド、イミダゾリジノン等があり、これらに限定されるものではないが、特に本発明においてはグリセリンがメインの乾燥防止剤の場合に最も優れた乾燥防止効果を示す。乾燥防止剤の使用量は、種類によって異なるが、通常、水100重量部に対して1~150重量部の範囲から適宜選択されるが、グリセリン及びそれに他の乾燥防止剤を併用したものを使用する場合には10~50重量部が好適である。

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【0028】また、上記水を必須とする水性媒体には、必要に応じてジェット噴射して付着したインクを紙によりよく浸透させるために、浸透性付与剤として浸透性付与効果を示す水溶性有機溶媒を加えてもよい。かかる浸透性付与剤としてはエタノール、イソプロピルアルコール等の低級アルコール、ジエチレングリコール-N-ブチルエーテル等のグリコールエーテル等を用いることができるが、これらに限定されるものではない。浸透性付与剤の使用量は、本発明における効果を達成すれば特に規定されないが、最終的に得られる水性インク中で0.1~10重量%となるような量が好ましい。

【0029】本発明の水性インクには、必要に応じて水溶性樹脂、pH調整剤、分散・消泡・紙への浸透のための界面活性剤、防腐剤、キレート剤等の添加剤を加えることができる。これら添加剤は、予め水性媒体中に添加しても、着色剤を含む自己水分散性樹脂溶液と水性媒体とを混合するときに添加しても、また、それらの混合後に添加してもよいが、好ましくは最終ろ過後の添加剤の添加は避けたほうがよい。

【0030】本発明でのインクジェット記録用水性インクは、前記したように好ましくは転相乳化法によって得られる。即ち、第1段階として塩基(b)で中和された合成樹脂(a)を含む溶液に着色剤が分散または溶解した着色ミルベースを作成する。第2段階として、第1段階で得られた着色ミルベースを過剰量の水性媒体と混合させることにより、着色剤を内包する水分散性樹脂粒子を得るカプセル化工程を実施する。当該水性インクの製造にあたっては、第3段階として、インクジェット記録用水性インク中のカプセル粒子の分散安定性を高めるために、第1段階のミルベース工程で用いた有機溶媒を除去する脱溶媒工程を入れるのが好ましい。この脱溶媒工程において必要なら水を除去してもよい。また勿論、この第3段階の工程は場合によっては省くこともある。尚、第2または3段階の工程が終了した後、フィルターろ過や遠心分離等で大粒径粒子を除去する工程を行うことが好ましい。

【0031】

【実施例】次に実施例及び比較例を挙げて本発明を更に具体的に説明する。尚、以下の実施例中における「部」は『重量部』を表わす。

(ミルベース例1)

カーボンブラック	20部
スチレンアクリル酸樹脂	20部
(スチレン/メタアクリル酸メチル/アクリル酸ブチル/アクリル酸/アクリル酸2-エチルヘキシル=60/20/10/7/3; 分子量2万・酸価55・ガラス転移温度68℃)	
メチルエチルケトン	60部
ガラスビーズ	150部

の配合物をペイントシェーカーで4時間練肉し、

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メチルエチルケトン	30部
イソプロピルアルコール	40部

を加えて内容物を取り出し、ミルベース溶液170部を得た。

(ミルベース例2)

カーボンブラック	20部
スチレンアクリル酸樹脂	20部
(スチレン/メタアクリル酸メチル/メタアクリル酸/アクリル酸2-エチルヘキシル=59/15/15/11; 分子量4万・酸価100・ガラス転移温度60℃)	
メチルエチルケトン	60部
ガラスビーズ	150部

の配合物をペイントシェーカーで4時間練肉し、メチルエチルケトン30部、イソプロピルアルコール40部を加えて内容物を取り出し、ミルベース溶液170部を得た。

(ミルベース例3)

カーボンブラック	20部
スチレンアクリル酸樹脂	20部
(スチレン/アクリル酸/メタアクリル酸=65/10/25; 分子量4万5千・酸価241・ガラス転移温度116℃)	
メチルエチルケトン	50部
ガラスビーズ	150部

の配合物をペイントシェーカーで4時間練肉し、メチルエチルケトン40部、イソプロピルアルコール40部を加えて内容物を取り出し、ミルベース溶液170部を得た。

(実施例1) ミルベース例1のミルベース170部にN-メチルジエタノールアミン2.1部(樹脂の中和率90%相当)を加えを攪拌しながら、グリセリン200部とイオン交換水600部の混合液を毎分5mlの速度で滴下し、着色マイクロカプセルを得た。得られたカプセル液をロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終の着色マイクロカプセル水分散物を得た。この水分散物を3μmフィルターを用いてろ過を行い、インクジェット記録用水性インクとした。

【0032】得られた水性インク中のマイクロカプセルは0.23μmの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を示し、インクジェットプリンターを用いた印字は安定しており、得られた印刷物は滲みもなく、耐水耐光性に優れていた。

【0033】ミルベース例1からカーボンブラックを除いた樹脂溶液にN-メチルジエタノールアミンを中和率100%相当加え、同様にして水を滴下、樹脂の自己分散乳化液を得た結果、分散物の平均粒子径は0.51μmであった。

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(実施例2) ミルベース例2のミルベース170部にN-メチルジエタノールアミン2.9部(樹脂の中和率68%相当)を加えを攪拌しながら、グリセリン200部とイオン交換水600部の混合液を毎分5mlの速度で滴下し、着色マイクロカプセルを得た。得られたカプセル液をロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終の着色マイクロカプセル水分散物を得た。この得られたマイクロカプセル水分散物にグリセリン200部を加え、攪拌後3 $\mu$ mフィルターを用いてろ過を行い、インクジェ

【0034】得られた水性インク中のマイクロカプセルは0.21 $\mu$ mの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を示し、インクジェットプリンターを用いた印字は安定しており、得られた印刷物は滲みもなく、耐水耐光性に優れていた。

【0035】ミルベース例2からカーボンブラックを除いた樹脂溶液にN-メチルジエタノールアミンを中和率100%相当加え、同様にして水を滴下、樹脂の自己分散乳化液を得た結果、分散物の平均粒子径は0.52 $\mu$ mであった。

(実施例3) ミルベース例3のミルベース170部にトリエタノールアミン11.7部(樹脂の中和率100%相当)を加え、攪拌しながらグリセリン80部とイオン交換水300部の混合液を毎分5mlの速度で滴下し、着色マイクロカプセル前駆液(凝集分散物)を得た。得られたカプセル前駆液をガラスビーズを分散メディアとするペイントシェーカーを用いて1時間分散し、その後グリセリン80部とイオン交換水300部の混合液を毎分5mlの速度で滴下しカプセル液を得た。得られたカプセル液をロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終の着色マイクロカプセル水分散物を得た後、1.2 $\mu$ mフ

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ィルターを用いてろ過を行い、インクジェット記録用水性インクとした。

【0036】得られた水性インク中のマイクロカプセルは0.10 $\mu$ mの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を示し、インクジェットプリンターを用いた印字は安定しており、得られた印刷物は滲みもなく、耐水耐光性に優れていた。

【0037】(比較例1) 特開平3-221137号公報の樹脂A-3(酸価:固形分相当40)を用いた実施例6(トリエチルアミン中和率48.5%)のマイクロカプセル水分散物にグリセリン60部を加え、攪拌した後3 $\mu$ mフィルターを用いてろ過を行い、インクジェット記録用インクとした。得られた水性インク中のマイクロカプセルは0.7 $\mu$ mの平均粒子径を有しており、長期の保管では容器の底に目視可能な凝集物が存在しており、インクジェットプリンターを用いた印字は不安定であった。

【0038】(比較例2) ミルベース例3の樹脂の代わりにスチレンモノマー/アクリル酸モノマー/メタアクリル酸モノマー=55/15/30;酸価310・ガラス転移温度119℃のスチレンアクリル樹脂を用いて、ミルベース化し、このミルベース170部にトリエタノールアミン16.5部(樹脂の中和率100%相当)を加えた、実施例3と同様の方法でカプセル化を試みたが、行程の途中で凝集して微粒径で安定したマイクロカプセルは得られなかった。

【0039】

【発明の効果】本発明のインクジェット記録用水性インクは、印刷品質・耐水性・耐光性に優れた樹脂分散型水性インクの特長を殺すことなく、分散安定性に優れ、かつノズル目詰まりもなく、安定したインクジェット噴射特性を可能にする。

## PATENT ABSTRACTS OF JAPAN

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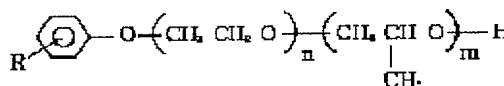
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## (54) WATER-BASE DISPERSED INK FOR BUBBLE-JET RECORDING AND INK-JET RECORDING AND APPARATUS USING THE INK

(57)Abstract:

PURPOSE: To obtain the subject ink containing water, a water-soluble organic solvent composed of a compound having a specific structure and a pigment dispersion dispersed by using a specific dispersing agent, having excellent storage stability and enabling stable ejection through a nozzle.

CONSTITUTION: This water-base dispersed ink contains at least (A) water, (B) a water-soluble organic solvent composed of a compound of the formula (R is H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub> or Cl; (n) is an integer of 4-20) and (C) a dispersion of a pigment or a disperse dye produced by dispersing a pigment or a disperse dye with a polymeric dispersing agent having an anionic dissociation group. The addition amount of the component B is 1-30wt.%, preferably 3-20wt.% based on the ink. The polymeric dispersing agent preferably has a weight-average molecular weight of 3,000-1,5000 and the weight ratio of (coloring material) : (dispersing agent) is 10:3 to 10:0.5 for the pigment and 1:3 to 20:1 for the disperse dye.



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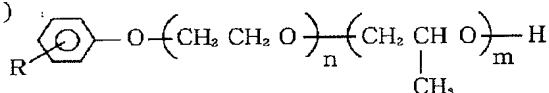
## CLAIMS

[Claim(s)]

[Claim 1]In drainage system distribution ink containing a pigment dispersion object or a disperse dye dispersing element which carried out the distributed processing of water, a water soluble organic solvent, paints, or the disperse dye using a dispersing agent at least, Bubble jet water-system distribution ink which said dispersing agent is a polymers dispersing agent which has an anionic dissociable group, and is characterized by said water soluble organic solvent consisting of a compound shown by following general formula (I).

[Formula 1]

一般式 (I)



(R shows H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, or Cl among a formula, and n shows the integer of 4-20.) m shows the integer of 0-2.

[Claim 2]An ink jet recording method applying said ink according to claim 1 as said ink in an ink jet recording method which records by making an ink droplet formed with an inkjet method adhere to a recorded material.

[Claim 3]The ink jet recording method according to claim 2 in which said inkjet method is a method which makes thermal energy act on ink.

[Claim 4]The ink jet recording method according to claim 2 which breathes out and records ink from a recording head using film boiling of a thin film heater as a source of regurgitation energy generation.

[Claim 5]An ink cartridge applying said ink according to claim 1 as said ink in an ink cartridge which has the ink seat part which accommodated ink.

[Claim 6]A recording unit applying said ink according to claim 1 as said ink in a recording unit which has both the head sections for making into an ink droplet an ink seat part which accommodated ink, and said ink, and carrying out the regurgitation.

[Claim 7]The recording unit according to claim 6 which makes thermal energy act on said ink, and performs ink discharge in said head section.

[Claim 8]An ink-jet recording device having said ink cartridge according to any one of claims 5 to 7 or a recording unit in an ink-jet recording device which records by making an ink droplet formed with an inkjet method adhere to a recorded material.

[Translation done.]

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## DETAILED DESCRIPTION

### [Detailed Description of the Invention]

#### [0001]

[Industrial Application]This invention relates to the ink jet recording method and recorder using the bubble jet water-system distribution ink and this which used paints or a disperse dye. It excels in the discharging performance in the ink-jet recording device of Bubble Jet in more detail, The record paper which has the absorptivity of drainage system ink, i.e., inkjet printing paper, What is called regular papers, such as paper of fine quality, a copy paper, a letter paper, a hot printing paper, and business form paper for wire dot printers, And the recording medium and concrete target having the absorptivity of drainage system ink are received at inkjet printing paper, a film, cloth, the metal by which ground treatment was carried out, a plastic, etc., Color grace is high and is related with the ink jet recording method and recorder using the ink-jet-recording ink and this which give the recorded image excellent in robustness.

#### [0002]

[Description of the Prior Art]In recent years, aqueous pigment dispersion has come to be used for pens and pencils as ink. It is because the purpose is best material system that gives robustness, such as a water resisting property and lightfastness. As a background of this, there is development of the drainage system particle dispersion techniques of paints, fat dye, and a disperse dye. The trial which applies the pigment dispersion art in which long-term preservation stability is securable to an ink jet also progresses, and it is coming by such hypoviscosity.

[0003]However, in the method which makes it recording principles to give momentarily high heat directly to ink like Bubble Jet, to boil ink itself, and to consider it as drop formation and regurgitation energy. There was big difficulty in using the dispersing element obtained by the above-mentioned dispersion techniques as ink for bubble jets only by it. The reason is that a dispersing element condenses on the heating element of a recording head directly. Therefore, even if condensation was controlled or having been condensed by a certain means, the material and the means which the regurgitation is maintainable, or the device device was required. In the organic color and the disperse dye, itself was also difficult for distributing to 0.2micro or the particles not more than it with mean particle diameter, and it was especially required for the grain size which can reach in an industrial meaning to have restriction, and to give regurgitation durability under the conditions.

[0004]On the other hand, as aqueous pigment ink for ink jets, the invention of JP,2-255875,A, JP,4-334870,A, JP,4-57859,A, JP,4-57860,A, etc. is indicated. However, the aqueous pigment ink concerning these inventions is not enough as ink which solves a technical problem called particle distribution of an organic color or a disperse dye, and the dischargeability in those Bubble Jet.

[0005]In an ink jet water-based ink in JP,62-14188,B, If the compound which consists of polyethylene-glycol phenyl ether and its derivative is used, in the ink which uses a color, it shall be effective to the improvement of \*\*\*\* ball nature, and coexistence of drying property (perviousness to paper), and a blot. And it is supposed that the solubility to water is the compound used by this invention 2 to 3% or less at a room temperature.

#### [0006]

[Problem(s) to be Solved by the Invention]This invention reaches in view of the above-

mentioned conventional technology, and it is ink using a pigment dispersion object or a disperse dye dispersing element. It excels in preservation stability and aims at providing the bubble jet water-system distribution ink which can perform the stable regurgitation in a bubble jet recorder.

[0007]When color recording is performed to a regular paper or textiles, this invention does not have a blot and generating of feathering, and is excellent in fixability, and is excellent in color enhancement, and an object of this invention is to provide the bubble jet water-system distribution ink in which the good printing quality of robustness is obtained.

[0008]An object of this invention is to provide the ink jet recording method, the apparatus, and the recorder which use the above-mentioned bubble jet water-system distribution ink.

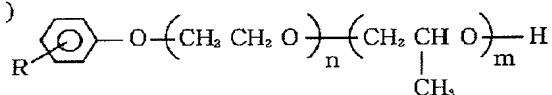
[0009]

[Means for Solving the Problem]Namely, in drainage system distribution ink in which this invention contains a pigment dispersion object or a disperse dye dispersing element which carried out the distributed processing of water, a water soluble organic solvent, paints, or the disperse dye using a dispersing agent at least, Said dispersing agent is a polymers dispersing agent which has an anionic dissociable group, and said water soluble organic solvent is bubble jet water-system distribution ink consisting of a compound shown by following general formula (I).

[0010]

[Formula 2]

一般式 (I)



(R shows H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, or Cl among a formula, and n shows the integer of 4-20.) m shows the integer of 0-2.

In the ink jet recording method which records by making the ink droplet formed with the inkjet method adhere to a recorded material, this invention is an ink jet recording method applying the bubble jet water-system distribution ink of a statement to the above as said ink.

[0011]This invention is an ink jet recording method which breathes out and records the bubble jet water-system distribution ink of a statement on the above from the recording head which used the film boiling of the thin film heater as a source of regurgitation energy generation.

[0012]In an ink cartridge which has the ink seat part which accommodated ink, this invention is an ink cartridge applying bubble jet water-system distribution ink of a statement to the above as said ink.

[0013]In a recording unit which has both the head sections for making into an ink droplet an ink seat part which accommodated ink, and said ink, and carrying out the regurgitation, this invention is a recording unit applying bubble jet water-system distribution ink of a statement to the above as said ink.

[0014]In an ink-jet recording device which records by making an ink droplet formed with an inkjet method adhere to a recorded material, this invention is an ink-jet recording device having an ink cartridge or a recording unit of a statement in the above.

[0015]Hereafter, this invention is explained in detail. Bubble jet water-system distribution ink (it is hereafter described as "drainage system distribution ink") of this invention has the feature in a place which enabled atomization to give discharging performance in Bubble Jet made difficult to difficult paints and a disperse dye in the above-mentioned conventional technology.

[0016]With a polymers dispersing agent which has an alkali meltable type anionic dissociable group, drainage system distribution ink of this invention carries out particle distribution of paints or the disperse dye, and uses it as a disperse dye dispersing element or a pigment dispersion object, and in order to give discharging performance, a new water soluble organic solvent is used indispensable.

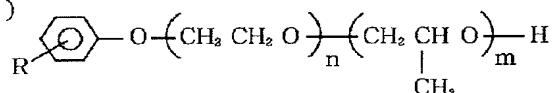
[0017]A water soluble organic solvent by which selection use is carried out by this invention consists of a compound which is phenol or an ethylene oxide addition compound of the derivative, and is shown by following general formula (I).



[0018]

[Formula 3]

一般式 (I)



[0019] R shows H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>, or Cl among a formula -- n -- 4-20 -- desirable -- 5-20 -- the integer of 10-18 is shown still more preferably. m shows the integer of 0-2. That is, the number of addition mols of ethylene oxide is 20 or less [ 4 or more ].

[0020] The compound shown by above general formula (I) has weak surface activity ability while having sufficient water solubility. Weak surface activity ability has referred to emulsification and solubilization power here. The long-term regurgitation durability in a bubble jet recording head is not acquired to the ink [ be / the number of addition mols of ethylene oxide / three or less ] using the dispersing element of the organic color or the disperse dye. The number of addition mols of desirable ethylene oxide is 5 mol or more. If the number of addition mols exceeds 20, the effect of improvement in regurgitation endurance will become small again.

[0021] Several meters addition mols of propylene oxide are 0-2, and viscosity of a compound of general formula (I) falls and it becomes easy to use them by addition of slight propylene oxide. As for m, in the case of n>=15, being referred to as 1-2 is preferred, and, as for m, 0-1 are especially preferred at n< 15.

[0022] Although a compound shown by general formula (I) which has comparatively long ethylene oxide chains is similar with the glycols used conventionally, it is intrinsically important for it that one end is phenol or its derivative. Performances, such as the emulsification and solubilization, are not shown at all by glycols, such as a polyoxyethylene of chain length of the same grade that a hydrophobic atom group needs for an end, or triethylene glycol. When a hydrophobic atom group of an end is the phenol by which alkylation was carried out, a carbon number of an alkyl group is two or less, and water solubility falls that it is more than it, and it is not preferred. As for phenol, what was replaced with chlorine is effective. When a substituent is PARAKURORU phenol, since water solubility becomes low, a long time is more nearly required for ethylene oxide chains than a case where it is not replaced, and five or more carbon numbers are preferably required for them.

[0023] The preservation stability of drainage system distribution ink is good, without drainage system distribution ink of this invention in which these water soluble organic solvents were added having an adverse effect on the stability of a polymers dispersing agent which has an anionic dissociable group of alkali solubility. Although a reason these water soluble organic solvents improve discharging performance does not come out in \*\*, the above-mentioned feature is considered to have been easy to remove distributed destruction which occurred thermally, i.e., particle condensation, and its deposition from a heater surface, and to act on a heater.

[0024] A compound shown by general formula (I) in this invention has solubility as high as 5 to 50% to water, in order to use it as a water soluble solvent.

[0025] An addition of a water soluble organic solvent in drainage system distribution ink of this invention is usually 3 to 20 % of the weight preferably one to 30% of the weight. Since viscosity will become high and frequency response nature will fall if moistness becomes insufficient at less than 1 % of the weight and 30 % of the weight is exceeded, it is not desirable.

[0026] In using carbon black as paints, a dispersing element with sufficient dischargeability may be obtained with a diameter of a granule only with a polymers dispersing agent, and, then, it does not necessarily need such a water soluble organic solvent. It has the effect of being useful also in textile printing of polyester fiber content textiles, and raising especially level dyeing nature again. [ of drainage system distribution ink of this invention ]

[0027] (Polymers dispersing agent) A polymers dispersing agent used for drainage system distribution ink of this invention is alkali meltable type water soluble resin, weight average molecular weight is 1000-30000, and ranges of it are 3000-15000 preferably. Specifically

Hydrophobic monomers, such as alkyl ester of styrene, a styrene derivative, vinyl naphthalene, a vinyl naphthalene derivative, and acrylic acid, and alkyl ester of methacrylic acid, They are copolymers which consist of hydrophilic monomers, such as alpha and beta-ethylenic unsaturated carboxylic acid and its aliphatic series alcohol ester, acrylic acid, methacrylic acid, maleic acid, itaconic acid, boletic acid, and those derivatives, and those salts.

[0028]As a base which forms a salt, they are alcohol amines, such as alkali metal ion, monoethanolamine, diethanolamine, and triethanolamine. A copolymer may have which structures, such as randomness, a block, and a graft. acid value -- 100-450 -- it is the range of 130-400 preferably.

[0029]As a polymers dispersing agent used for this invention, it is possible to also use water soluble resin, such as water-soluble polymer, such as polyvinyl alcohol and carboxymethyl cellulose, a naphthalene sulfonic acidformaldehyde condensate, and polystyrene sulfonate, further.

[0030]In this invention, a pigment dispersion object or a disperse dye dispersing element which carried out the distributed processing of paints or the disperse dye using a polymers dispersing agent is formed. In the case of a pigment dispersion object, a range of the amount of polymers dispersing agent used is 10:3 to 10:0.5 by weight of a weight:dispersing agent of paints. A fitness ratio is experimentally determined from viewpoints of mean particle diameter, viscosity, stability, distributed efficiency, etc. which may reach using selected paints and a polymers dispersing agent. As for quantity of a polymers dispersing agent which is adsorbing and dissolving in paints, in drainage system distribution ink of this invention used for a bubble jet recorder, it is preferred that it is 2 or less % of the weight in ink.

[0031]In the case of a disperse dye dispersing element, a range of the amount of polymers dispersing agent used is 1:3 to 20:1 by weight of a weight:dispersing agent of a disperse dye.

[0032](Base) A base is required in order to use a polymers dispersing agent used for ink of this invention in a drainage system. As a suitable base, therefore, ethanolamine, diethanolamine, Triethanolamine, N-methylethanol amine, N-ethyldiethanolamine, 2-amino-2-methylpropanol, 2-ethyl-2-amino-1,3-propanediol, Inorganic bases, such as organic bases, such as 2-(2-aminoethyl) ethanolamine, tris(hydroxymethyl) aminomethane, ammonia, piperidine, morpholine, and beta-dihydroxyethyl urea, sodium hydroxide, a potassium hydrate, and lithium hydroxide, are used.

[0033]Although optimal base species change with kinds of selected paints and dispersing agent, it is nonvolatile and stability and a high thing of water retention are preferred. From quantity calculated from acid value of a polymers dispersing agent, quantity of a base to be used is fundamentally used as an amount of bases required to neutralize it, respectively. A base of quantity which exceeds the equivalent of acid depending on the case may be used. It is performed for the purpose, such as improvement in dispersibility, pH adjustment of ink, adjustment of recording performance, and improvement in moistness.

[0034](Paints) As for quantity of paints contained in drainage system distribution ink used by this invention, it is preferred to use in 2 to 12% of the weight of the range preferably one to 20% of the weight to the whole ink.

[0035]As carbon black used for black ink, That in which specific surface area according [ primary particle diameter ] to 40mmicro and a BET adsorption method has 50-300m<sup>2</sup>/g from 15 by carbon black manufactured with the furnace method and a channel process, DBP oil absorption has 0.5 to 10% in 40-150 ml/100 g, and volatile matter content, and a pH value has 2-9 is preferred.

[0036]As those carbon black pigments (C. I.Pigment Black 7). \*\*No.2300, No.900, MCF-88, No.33, No.40, No.45, No.52, MA7, MA8, MA100, No.2200B (above Mitsubishi Kasei Corp. make), Raven 700, Raven 5750, Raven 5250, Raven 5000, Raven3500, Raven 1255 (above made in Colombia),

[0037]Regal 400R, Regal 330R, Regal 660R, Mogul L, Monarch 700, Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300, Monarch 1400 (above Cabot Corp. make), [0038]Color Black FW1, Color Black FW2, Color Black FW2V, Color Black FW18, Color Black FW200, Color Black S150, Color Black S 160, Color Black S170, Printex 35, Printex U,

Printex V, Printex 140U, Printex 140V, and Special Black 6, Special Black 5, Special Black 4A, Special Black 4 (above Degussa make), etc. can be used.

[0039]As paints used for yellow ink, C.I.Pigment Yellow 12, C.I.Pigment Yellow 13, C.I.Pigment Yellow 14, C.I.Pigment Yellow 16, C.I.Pigment Yellow 17, C.I. Pigment Yellow 73, C.I.Pigment Yellow 74, C.I.Pigment Yellow 75, C.I.Pigment Yellow 83, and C.I.Pigment Yellow. 108, C.I.Pigment Yellow 109, C.I.Pigment Yellow 110, C.I.Pigment Yellow180, C.I.Pigment Yellow 182, [0040]As paints used as magenta ink, C.I.Pigment Red 5, C.I.Pigment Red 7, C.I.Pigment Red 12, C.I.PigmentRed 112, C.I.Pigment Red 122, C.I.Pigment Red 123, C.I.Pigment Red 168, C.I.Pigment Red 184, C.I.Pigment Red 202, [0041]As paints used as cyan ink, C.I.Pigment Blue 1, C.I.Pigment Blue 2, C.I.Pigment Blue 3, C.I.Pigment Blue 15:3, C.I.Pigment Blue 16, C.I.Pigment Blue. 22, C.I.Pigment Blue60, C.I.Vat Blue 4, C.I.Vat Blue 60, etc. are mentioned.

[0042]When red, green, blue, and neutral colors above else are needed, it is preferred independent, to use together and to use the following paints. C.I.Pigment Red 209, C.I.Pigment Red 224, C.I.Pigment Red 177, C.I.Pigment Red 194, C.I.Pigment Orange 43, C.I.VatViolet 3, C.I.Pigment Violet. 19, C.I.Pigment Green 36, C.I.Pigment Green 7, C.I.Pigment Violet 23, C.I.Pigment Violet 37, C.I.Pigment Blue 15:6, [0043](Disperse dye) As for quantity of a disperse dye contained in drainage system distribution ink used by this invention, it is preferred to use in 1.5 to 20% of the weight of the range preferably one to 25% of the weight to the whole ink.

[0044]As a disperse dye to be used, they are the following compounds.

[0045]<Disperse Yellow Dye. >C.I.Disperse Yellow 5, C.I.Disperse Yellow 42, C.I.Disperse Yellow 54, C.I.Disperse Yellow 64, C.I.Disperse Yellow 79, C. I. Disperse Yellow82, C.I.Disperse Yellow 83, C.I.Disperse Yellow 93, C.I.Disperse Yellow 99, and C.I.Disperse. Yellow 100, C.I.Disperse Yellow 119, C.I.Disperse Yellow 122, C.I.Disperse Yellow 124, C.I.Disperse Yellow 126, C. I.Disperse Yellow160, C.I.Disperse Yellow 184:1, C.I.Disperse Yellow 186, C.I.Disperse Yellow 198, C.I.Disperse Yellow 199. , C.I.DisperseYellow 204, C.I.DisperseYellow 224, C.I.Disperse Yellow 237,

[0046]<Disperse Orange Dye> C.I.Disperse Orange 13, C.I.Disperse Orange 29, C.I.Disperse Orange 31:1, C.I.Disperse Orange 33, C. I.Disperse Orange 49, C.I.Disperse Orange54, C.I.Disperse Orange 55, C.I.Disperse Orange 66, C.I.DisperseOrange73, C.I. Disperse Orange 118, C.I.Disperse Orange 119, C.I.Disperse Orange 163, [0047]<Disperse. Red. Dye>C.I.Disperse Red54, C.I.Disperse Red 72, C.I.Disperse Red 73, C.I.Disperse Red 86, C.I.DisperseRed 88, C.I.Disperse Red 91 and C.I.Disperse. Red92 and C.I.Disperse. Red 93 and C.I.Disperse. Red 111 and C.I.Disperse. Red. 126, C.I.Disperse Red 127, C.I.Disperse Red 134, C.I.Disperse Red 135, C.I.Disperse Red 143, C.I.Disperse Red 145, C.I. Disperse Red 152, C.I.Disperse Red 153, C.I.Disperse Red 154, C.I.Disperse Red 159, and C.I.Disperse Red. 164, C.I.Disperse Red 167:1, C.I.Disperse Red 17 7 and C.I.Disperse Red. 181 and C.I.Disperse Red. 204 and C.I.Disperse Red. 206, C.I.Disperse Red 207, C.I.Disperse Red 221, C.I.Disperse Red239, C.I.Disperse Red 240, C.I.Disperse Red 258, C.I.Disperse Red 277 and C.I.Disperse. Red 278 and C.I.Disperse. Red 283 and C.I.Disperse. Red 311, C.I.Disperse Red 323, C.I.Disperse Red 343, C.I.Disperse Red 348, C.I.DisperseRed 356, C.I.Disperse Red 362, [0048]<Disperse Violet Dye > C.I.Disperse Violet 33,

[0049]<Disperse. Blue. Dye. >C.I.Disperse Blue 56, C.I.Disperse Blue 60, C.I.Disperse Blue 73, C.I.Disperse Blue 87, C.I.Disperse Blue 113, C.I. Disperse Blue 128, C.I.Disperse Blue 143, C.I.Disperse Blue 148, C.I.Disperse Blue 154, and C.I.Disperse. Blue. 158, C.I.Disperse Blue 165, C.I.Disperse Blue 165:1, C.I.DisperseBlue 165:2, C.I.Disperse Blue 176, C.I.Disperse Blue 183, C.I. DisperseBlue 185, C.I.Disperse Blue 197, C.I.Disperse Blue 198, C.I.Disperse Blue 201, and C.I.Disperse. Blue 214, C.I.Disperse Blue 224, C.I.Disperse Blue 225, C.I.Disperse Blue 257, C.I.Disperse Blue 266, C.I.Disperse Blue 267, C.I.Disperse Blue 287, C.I.DisperseBlue 354, C.I.Disperse Blue 358, C.I.Disperse Blue 365, C.I.Disperse Blue 368, [0050]<Disperse Green Dye>C.I.Disperse Green 6:1 and C.I.Disperse Green 9, are mentioned.

[0051]Among these colors, preferably, C.I.Disperse Yellow 5, C.I.Disperse Yellow 42, C.I.Disperse Yellow 83, C.I.Disperse Yellow 93, C.I.Disperse Yellow 99, C. I. Disperse Yellow 198, C.I.Disperse Yellow 224, C.I.Disperse Orange 29, C.I.Disperse Orange 49, and C.I.Disperse Orange 73, [0052] C.I.Disperse Red 92, C.I.Disperse Red 126, C.I.Disperse Red 145, C.I.Disperse Red 152, C.I.Disperse Red 159, C.I.Disperse Red 177 and C.I.Disperse. Red 181 and C.I.Disperse. Red 206 and C.I.Disperse. Red 283 and C.I.Disperse. Blue. 60, C.I.Disperse Blue 87, C.I.Disperse Blue 128,

C.I.Disperse Blue 154, C.I.Disperse Blue 201, C.I.Disperse Blue 214, C.I. They are compounds, such as Disperse Blue 224, C.I.Disperse Blue257, C.I.Disperse Blue 287, and C.I.Disperse Blue 368.

[0053]These colors are desirable examples, and it is not limited to seeing and they may be compounded [ these ] newly.

[0054](Solvent) As a solvent used for this invention, they are organic solvents with water and miscibility. If those solvents are classified, it can divide into the three following groups. \*\* moistness is high, and have at the end a solvent of the 1st group that is [ that it is hard to evaporate ] excellent in hydrophilic nature, and \*\* hydrophobic atom group, and wettability to the hydrophobic surface is also good -- evaporation drying property -- a solvent of a certain 2nd group, and \*\* -- it has moderate wettability and is a solvent (monohydric alcohol) of the 3rd group of hypoviscosity.

[0055]As a solvent belonging to the 1st group, \*\* Ethylene glycol, a diethylene glycol, Triethylene glycol, tripropylene glycol, glycerin, 1,2,4-butanetriol, 1,2,6-hexanetriol, 1,2,5-pentanetriol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, dimethylsulfo KISHIKIDO, diacetone alcohol, Glycerin monoallyl ether, propylene glycol, a butylene glycol, The polyethylene glycol 300, thiodiglycol, N-methyl-2-pyrrolidone, 2-pyrrolidone, gamma-butyrolactone, 1,3-dimethyl-2-imidazolidinone, Sulfolane, trimethylolpropane, trimethylolethane, neopentyl glycol, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether,

\*\*\*\*\*  
They are propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, beta-dihydroxyethyl urea, urea, acetonylacetone, pentaerythritol, 1,4-cyclohexanediol, etc.

[0056]As a solvent belonging to the 2nd group, \*\* Hexylene glycol, ethylene glycol monopropyl ether, Ethylene glycol monobutyl ether, ethylene glycol monoisobutyl ether, Ethylene glycol monophenyl ether, diethylene-glycol diethylether, Diethylene-glycol monobutyl ether, diethylene-glycol monoisobutyl ether, Triethylene glycol monobutyl ether, triethylene glycol wood ether, Triethylene glycol diethylether, tetraethylene glycol wood ether, Tetraethylene glycol diethylether, propylene glycol monobutyl ether, Dipropylene glycol monomethyl ether, dipropyleneglycol monopropyl ether, Dipropyleneglycol monobutyl ether, tripropylene glycol monomethyl ether, Glycerol monoacetate, glycerin diacetate, triacetin, ethylene glycol monomethyl ether acetate, diethylene-glycol-monomethyl-ether acetate, cyclohexanol, 1,2-cyclohexanediol, 1-butanol, It is 3-methyl-1,5-pentanediol, 3-hexene-2,5-diol, 2,3-butanediol, 1,5-pentanediol, 2, 4-pentanediol, 2, and 5-hexandiol etc.

[0057]\*\* As a solvent belonging to the 3rd group, they are ethanol, n-propanol, 2-propanol, 1-methoxy-2-propanol, furfuryl alcohol, tetrahydrofurfuryl alcohol, etc.

[0058]A kind or two sorts or more can be used for the above-mentioned solvent, choosing them suitably. A total amount of a water soluble solvent is 5 to 40 % of the weight to the whole ink in general.

[0059](Other additives) In drainage system distribution ink of this invention, it is possible as other additives to add a pH adjuster, an antiseptic, etc., for example. As a commercial antiseptic stable in a basic field, and effective, pro KUSERU (Zeneka Britain) etc. are typical.

[0060]When the basic physical properties of ink which comprises above materials are summarized, 80-150 nm of viscosity:2-6cps, surface tension:35 - 55 dyn/cm, pH:7.0-10.0, and mean particle diameter of 80-200 nm is the range of 80-120 nm more preferably. The amount of dispersing element solid content in ink is 1.5 to 20% of the weight of a range preferably one to 25% of the weight in general.

[0061]Content of water in ink is usually 25 to 87% of the weight of a range preferably ten to 93% of the weight.

[0062]Next, the method of preparation of drainage system distribution ink of this invention is explained.

(Atomization of a pigment dispersion object or a disperse dye dispersing element) First, the distributed processing of a water soluble organic solvent, paints, or the disperse dye is carried out using a polymers dispersing agent, and a particle dispersing element of a pigment dispersion object or a disperse dye dispersing element is obtained. The following methods are taken using

material of this invention to obtain a particle dispersing element.

[0063] A pre mixing process is performed in an anionic system polymers dispersing agent solution which has an anionic dissociable group for a wet cake of paints or a disperse dye, it mills with a dispersion device of a high shear rate succeeding, and in order to remove a coarse particle, centrifugal separation treatment is performed. When the target particle diameter is not obtained with sufficient yield with one sort of dispersion devices at this time, it is also effective to use together several sorts of dispersion devices. It is effective to combine a method of using device mixes of a high velocity revolution over 10,000 rpm, a method of making a dispersing agent solution into a jet and making paints contact at high speed or ultrasonic dispersion, and a bead mill not using a bead.

[0064] Then, material for a desired ink formula is added, temperature up is carried out to 35-50 \*\* depending on the case, and aging processing is performed. Centrifugal separation treatment for obtaining desired mean particle diameter eventually after an appropriate time, pressure filtration, etc. are performed. However, a polymers dispersing agent or a surface-active agent is made to live together at the time of color material composition in the case of an organic color and a disperse dye in which it is difficult to use a diameter of a granule, It is effective to use a raw material of a wet cake state which a polymers dispersing agent or a surface-active agent is made to contact in a method of controlling crystal growth and making it into a diameter of a granule or a stage of a synthetic reaction being completed and depositing a crystal, and crystal growth is controlled, and is a diameter of a granule, and improved wettability.

[0065] (Preparation of drainage system distribution ink) Particles of a pigment dispersion object acquired by performing it above, or a disperse dye dispersing element, Water, a water soluble organic solvent which consists of a compound shown by general formula (I), an organic solvent with other water and miscibility, and if needed, the specified quantity is blended, other additive agents are agitated respectively, it distributes uniformly, and drainage system distribution ink of this invention is obtained.

[0066] Drainage system distribution ink of this invention is the ink which used an above-mentioned disperse dye dispersing element or organic pigment dispersions, and is bubble jet water-system distribution ink which can perform stable regurgitation in a bubble jet recorder, namely, can answer a several rounds drive wave number in 3 kHz - 6 kHz.

[0067] Drainage system distribution ink of this invention is applicable to a design towards all uses that use a disperse dye or paints for record using Bubble Jet. Specifically, they are stationery, a color printer, a color plotter, poster printing, signboard printing, implant printing, textile printing, a light filter for liquid crystal displays, etc.

[0068] As a suitable method to record using ink of this invention, and a device, thermal energy corresponding to a record signal is given to indoor ink of a recording head, and a method and a device which are made to generate a drop with this thermal energy are mentioned.

[0069] An example of a head configuration which is the principal part of the device is shown in drawing 1, drawing 2, and drawing 3. The head 13 is obtained by sticking glass, ceramics or a plastic sheet etc. which has the slot 14 which lets ink pass, and the exothermic head 15 (although a head is shown by a diagram, not limited to this) used for thermal recording. The exothermic head 15 comprises the good substrate 20 of heat dissipation nature, such as the heating resistor layer 18 formed with the protective film 16 in which silicon oxide etc. are made to form, the aluminum electrode 17-1 and 17-2, Nichrome, etc., the accumulation layer 19, and alumina.

[0070] The ink 21 is coming to the regurgitation orifice (micropore) 22, and forms the meniscus 23 with an unillustrated pressure. If an electrical signal is added to the electrode 17-1 and 17-2 now, a field shown by n of the exothermic head 15 will generate heat rapidly, It is generated by air bubbles in the ink 21 which has touched here, the meniscus 23 projects by the pressure, and the ink 21 breathes out, and from the orifice 22, it becomes the record glob 24 and flies toward the recorded material 25.

[0071] An outline view of a multi head which put in order many heads shown in drawing 1 is shown in drawing 3. This multi head sticks the same exothermic head 28 as the glass plate 27 which has the multi-slot 26, and a thing explained to drawing 1, and is manufactured. Drawing 1

is a sectional view of the head 13 along an ink passage, and drawing 2 is a cutting plane in an A-B line of drawing 1.

[0072]One example of an ink-jet recording device incorporating this head is shown in drawing 4. In drawing 4, 61 is a braid as a wiping member, and the end is held by a braid attachment component, turns into a fixed end, and makes a gestalt of a cantilever. The braid 61 is allocated by position which adjoined a record section by a recording head.

[0073]In this example, it is held with a gestalt projected in moving trucking of a recording head. 62 is a cap, it is allocated in a home position which adjoins the braid 61, moves in the direction vertical to the move direction of a recording head, contacts a discharge opening surface, and possesses composition which caps. Further 63 is an ink absorber which adjoins the braid 61 and is allocated, and is held like the braid 61 with a gestalt projected in moving trucking of a recording head. The regurgitation recovering part 64 is constituted by the above-mentioned braid 61, the cap 62, and the absorber 63, and removal of moisture of an ink discharge opening face, dust, etc. is performed by the braid 61 and the absorber 63.

[0074]It is a recording head which records on a recorded material which counters a discharge opening surface which 65 has a regurgitation energy generation means and allotted a delivery by breathing out ink, and 66 is a carriage for carrying this recording head 65 and moving the recording head 65. The carriage 66 engaged with the guide shaft 67 slidably, and has connected some carriages 66 with the belt 69 driven by the motor 68 (un-illustrating). Thereby, movement of the carriage 66 is attained along with the guide shaft 67, and it becomes movable [ a record section by the recording head 65, and its adjoining field ].

[0075]51 is a feeding part for inserting a recorded material, and 52 is a paper feed roller driven by an unillustrated motor. Paper is delivered to a delivery unit which arranged the paper ejecting roller 53 as a recorded material is fed to a discharge opening surface of a recording head, and a position which counters by these composition and record advances by it.

[0076]In the above-mentioned composition, when the recording head 65 returns to a home position by end of record, etc., the cap 62 of the head recovering part 64 is evacuated from moving trucking of the recording head 65, but the braid 61 is projected in moving trucking. As a result, wiping of the discharge opening surface of the recording head 65 is carried out. When the cap 62 caps in contact with a regurgitation side of the recording head 65, the cap 62 moves so that it may project in moving trucking of a recording head.

[0077]When the recording head 65 moves to a recording start position from a home position, the cap 62 and the braid 61 are in the same position as a position at the time of the above-mentioned wiping. As a result, also in this movement, wiping of the discharge opening surface of the recording head 65 is carried out.

[0078]Movement at a home position of the above-mentioned recording head moves to a home position which adjoined a record section at the predetermined intervals, not only the time of an end of record, and regurgitation recovery but while moving in a record section for record of a recording head, and the above-mentioned wiping is performed with this movement.

[0079]Drawing 5 is a figure showing an example of an ink cartridge which accommodated ink supplied to a head via an ink supply member, for example, a tube. 40 is an ink stowage in which ink for supply was accommodated, for example, an ink bag, and the plug 42 made of rubber is formed at the tip here. By inserting a needle (un-illustrating) in this plug 42, ink in the ink bag 40 is closed, if supply on a head is possible. 44 is an ink absorber which receives waste ink. Especially as an ink seat part, it is preferred for this invention polio REFUFIN and that a liquid-facing surface with ink is formed with polyethylene.

[0080]\*\*\*\* which a head and an ink cartridge like the above show to not only a thing used as a different body but drawing 6 as an ink-jet recording device used by this invention -- it is used suitably also for that with which they were united.

[0081]In drawing 6, 70 is a recording unit, an ink seat part which accommodated ink into this, for example, an ink absorber, is stored, and ink in this ink absorber has composition breathed out as an ink droplet from the head section 71 which has two or more orifices. As a material of an ink absorber, it is preferred for this invention to use polyurethane.

[0082]72 is an air communicating port for making the atmosphere open an inside of a recording

unit for free passage. This recording unit 70 is replaced with and used for a recording head shown by drawing 4, and attachment and detachment of it are attained to the carriage 66.  
[0083]

[Example]Next, an example is given and this invention is explained concretely. The value which expressed that a part was a weight percentage with the following explanation, and weight average molecular weight measured by the GPC method which made styrene polymer the standard, and mean particle diameter are the numerical values measured by dynamic light scattering.

[0084]the example 1 [black ink B-1] anionic system polymers P-1 (styrene methacrylic acid-ethyl acrylate: -- the acid value 400, the weight average molecular weight 6000, and the solution of 20 % of the weight of solid content.) Neutralizer: The following carbon black dispersing elements B-1 were created, using monoethanolamine as a polymers dispersing agent.

[0085]

40 copies of P-dispersing element B-11 solution (20 % of the weight of solid content) carbon black MA100 (made by Mitsubishi Kasei Corp.) 24-copy ethylene glycol 20-copy water 116 copies[0086]Such materials were taught to the batch type vertical mold sand mill (made by eye MEKKUSU), and distributed processing was performed for 3 hours, having been filled up with the glass bead of the diameter of 1 mm as media, and water-cooling it. The viscosity of the liquid after distribution was 9 cps, and pH was 10.0. These dispersion liquid were covered over the centrifuge, the coarse particle was removed, and mean-particle-diameter 135mmicro and the dispersing element B-1 of 13% of solid content were obtained.

[0087]

5 mol of ethylene oxide addition compound ten-copy glycerin ten-copy isopropyl alcohol three-copy water of ink dispersing element B-1 (13% of solid content) 50-copy phenol 27 copies are added. It fully agitated and the viscosity of 3.2 cps, surface tension 45 dyn/cm, and the black ink jet ink B-1 of pH 10.0 were obtained.

[0088]the example 2 [yellow ink Y-2] anionic system polymers P-2 (styrene acrylic acid-methylmetaacrylate: -- the acid value 280, the weight average molecular weight 11000, and the solution of 20 % of the weight of solid content.) Neutralizer: The following yellow dispersing elements Y-2 were created, using diethanolamine as a dispersing agent.

[0089]

35 copies of P-dispersing element Y-22 solution (20 % of the weight of solid content) pigment yellow 74 Distributed processing was performed like the 25-copy ethylene glycol 15-copy water 125 or less copy example 1, and mean-particle-diameter 125mmicro and the dispersing element Y-2 of 15% of solid content were obtained.

[0090]

10 copies of 10 mol of ethylene oxide addition compound ten-copy glycerin isopropyl alcohol three-copy water of ink Y-2 dispersing-element Y-2 (15% of solid content) 50-copy phenol Carry out 27 copies in this way, and Viscosity of 2.8 cps, Surface tension 44 dyn/cm and the yellow color ink jet ink Y-2 of pH 9.5 were obtained.

[0091]The following yellow dispersing elements Y-3 were created using the example 3 [yellow ink Y-3] anionic system polymers P-3 (styrene acrylic acid-n-butyl acrylate: the acid value 360, the weight average molecular weight 9000, solution of 20 % of the weight of solid content, neutralizer:morpholine) as a dispersing agent.

[0092]

35 copies of P-dispersing element Y-33 solution (20 % of the weight of solid content) pigment yellow 109 Distributed processing was performed like the 24-copy ethylene glycol six-copy water 135 or less copy example 1, and the dispersing element Y-3 of mean-particle-diameter 120mmicro was obtained.

[0093]

Fully agitate the 5 mol of ethylene oxide addition compound ten-copy glycerin ten-copy diethylene-glycol seven-copy water 23-copy above-mentioned ingredient of ink Y-3 dispersing-element Y-3 (15% of solid content) 50 copy para clo RUFÉ Norian, and The viscosity of 3.2 cps, surface tension 46 dyn/cm, The yellow color ink jet ink Y-3 of pH 9.5 was obtained.

[0094]The following cyan color dispersing elements C-4 were created using the example 4 [cyan ink C-4] anionic system polymers P-1 as a dispersing agent like Example 1.

[0095]

30 copies of P-dispersing element C-41 solution (20 % of the weight of solid content) pigment blue 15:3 24 copies (fast gene blue FGF, the Dainippon Ink chemicals company make)

Distributed processing was performed like the ethanol 11-copy water 135 or less copy example 1, and mean-particle-diameter 120mmicro and the dispersing element C-4 of 15% of solid content were obtained.

[0096]

4 mol of ethylene oxide addition compound ten-copy glycerin ten-copy diethylene-glycol seven-copy water of ink C-4 dispersing-element C-4 (15% of solid content) 50 copy para methyl phenol Fully agitate the material of 23 or more copies, and Viscosity of 3.3 cps, surface tension 47 dyn/cm, The cyan color ink jet ink C-4 of pH 9.6 was obtained.

[0097]Using the example 5 [magenta ink M-5] anionic system polymers P-1 as a dispersing agent, the pigment red 122 (made by the Dainippon Ink chemicals company) was distributed like Example 1, and the magenta chromatism object M-5 was created. The mean particle diameter of this dispersing element was 145mmicro and 18% of solid content.

[0098]

M-ink 5 dispersing element M-5 20 mol of ethylene oxide addition compound 15-copy N-methyl-pyrrolidone ten-copy training ethylene-glycol-monomethyl-ether five-copy water of 40 copy para clo RUF Norian Fully agitate the material of 30 or more copies, and Viscosity of 3.5 cps, Surface tension 43 dyn/cm and the magenta color ink jet ink M-5 of pH 9.4 were obtained.

[0099]It distributed like Example 2, using the example 6[disperse dye blue ink BL-6] anionic-system polymers P-2 as a dispersing agent, and blue chromatism object BL-6 of the following was created.

[0100]

20 copies of P-dispersing element BL-62 solution (20 % of the weight of solid content) C.I. day sparse blue 79 wet cake 32 copies (solid content)

The mean particle diameter of the powder object was 125mmicro and 17% of solid content diethylene-glycol 15-copy water 141-copy at this rate.

[0101]

15 mol of ethylene oxide addition compound seven-copy water of ink BL-6 dispersing-element BL-6 (17% of solid content) 50-copy glycerin 15-copy phenol Fully agitate 28 copies of ingredients of these, and Viscosity of 2.5 cps, Surface tension 43 dyn/cm and blue color ink-jet-ink BL-6 of pH 9.7 were obtained.

[0102]the example 7 [disperse dye red ink R-7] anionic system polymers P-5 (styrene acrylic acid-ethyl acrylate: -- the acid value 250, the weight average molecular weight 13000, and the solution of 20 % of the weight of solid content.) Neutralizer: The following red chromatism objects R-7 were created, using aminomethyl propanol as a dispersing agent.

[0103]

the 20 copies of P-dispersing element R-75 solution (20 % of the weight of solid content) C.I. day sparse red 158 -- wet -- cake 24 copy (solid content)

Distributed processing was performed like the isopropyl alcohol ten-copy water 146 or less copy example 1, and mean-particle-diameter 115mmicro and the dispersing element R-7 of 13.5% of solid content were obtained.

[0104]

R-ink 7 dispersing element R-7 15 mol of ethylene oxide addition compound ten-copy ethylene glycol diethylether five-copy water of 40-copy thiodiglycol 16-copy ethylphenol Fully agitate 29 copies of ingredients of these, and Viscosity of 3.0 cps, surface tension 47 dyn/cm, The red color ink jet ink R-8 of pH 9.6 was obtained. The solid content of the last preparation things was about 5 % of the weight.

[0105]The example 8 [disperse dye yellow ink Y-8] anionic system polymers P-5 (styrene maleic-acid-n-butyl acrylate: the acid value 210, the weight average molecular weight 7000, solution neutralizer:triethanolamine of 20 % of the weight of solid content) are used as a



dispersing agent, The following yellow dispersing elements Y-8 were created.

[0106]

15 copies of P-dispersing element Y-85 solution (20 % of the weight of solid content) C.I. day sparse yellow 64 wet cake 28 copies (solid content)

Distributed processing was performed like the example 1 of an ethylene glycol 20-copy water 137 or less copy experiment, and mean-particle-diameter 136mmicro and the dispersing element Y-8 of 15% of solid content were obtained.

[0107]

Y-ink 8 dispersing element Y-8 4 mol of ethylene oxide addition compound ten-copy thio jig record ten-copy glycerin of 45-copy phenol Fully agitate five copies of ingredients of these, and Viscosity of 2.7 cps, Surface tension 51 dyn/cm and the yellow color ink JIETO ink Y-8 of pH 9.2 were obtained.

[0108]The following magenta chromatism objects M-9 were created using the solution of the monoethanolamine salt of the example 9 [magenta color ink M-9] anionic system polymers P-5 (styrene maleic-acid-n-butyl acrylate: the acid value 210, weight average molecular weight 7000) as a dispersing agent.

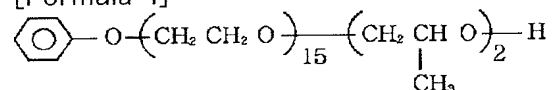
[0109]

15 copies of P-dispersing element M-95 solution (20 % of the weight of solid content) Scarlett F2B-02 paste 30-copy ethylene glycol ten-copy water The 130 copy above-mentioned material is pre mixed well, Distributed processing was performed like Example 1 and mean-particle-diameter 128mmicro and the dispersing element M-9 of 9.0% of solid content were obtained.

[0110]

M-ink 9 dispersing element M-9 15 mol of ethylene oxide and ten copies of 2 mol of propylene oxide addition compounds (compound of the following structure) of 60-copy phenol[0111]

[Formula 4]



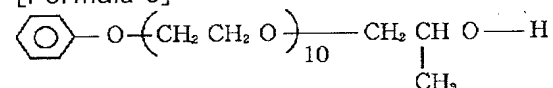
[0112]

Glycerin seven-copy ethylene glycol ten-copy isopropyl alcohol four-copy water Agitation mixing of nine copies of ingredients of these was fully carried out, and the viscosity of 2.7 cps, surface tension 47 dyn/cm, and the magenta color ink jet ink M-9 of pH 8.8 were obtained.

[0113]

M-ink 10 dispersing element M-9 10 mol of ethylene oxide and eight copies of 1 mol of propylene oxide addition compounds (compound of the following structure) of 60-copy phenol[0114]

[Formula 5]



[0115]

Thiodiglycol 13-copy glycerin ten-copy water Agitation mixing of nine copies of ingredients of these was fully carried out, and the viscosity of 2.4 cps, surface tension 55 dyn/cm, and the magenta color ink JIETO ink M-10 of pH 8.9 were obtained.

[0116]In the ink Y-2 of the comparative example 1 [comparative example ink CY-1] example 2, the ink which used the diethylene glycol instead of 10 mol of ethylene oxide addition compound of phenol was created, and it was referred to as comparative example ink CY-1.

[0117]In the ink Y-3 of the comparative example 2 [comparative example ink CY-2] example 3, the ink which used ethylene glycol instead of 5 mol of ethylene oxide addition compound of PARAKURORU phenol was created, and it was referred to as comparative example ink CY-2.

[0118]in the ink C-4 of the comparative example 3 [comparative example ink CC-3] example 4, glycerin was used instead of 4 mol of ethylene oxide addition compound of PARAME chill phenol -- ink creation was carried out and it was referred to as comparative example ink CC-3.

[0119]In ink BL-6 of the comparative example 4 [comparative example ink CBL-4] example 6,

the ink which used triethylene glycol instead of 15 mol of ethylene oxide addition compound of phenol was created, and it was referred to as comparative example ink CBL-4.

[0120]In the ink Y-2 of the comparative example 5 [comparative example ink CY-5] example 2, the ink which used 3 mol of ethylene oxide addition compound of phenol instead of 10 mol of ethylene oxide addition compound of phenol was created, and it was referred to as comparative example ink CY-5.

[0121]In the ink Y-3 of the comparative example 6 [comparative example ink CY-6] example 3, the ink which used 3 mol of ethylene oxide addition compound of PARAKURORU phenol instead of 5 mol of ethylene oxide addition compound of PARAKURORU phenol was created, and it was referred to as comparative example ink CY-6.

[0122]in the ink C-4 of the comparative example 7 [comparative example ink CC-7] example 4, 30 mol of ethylene oxide addition compound of PARAME chill phenol was used instead of 4 mol of ethylene oxide addition compound of PARAME chill phenol. — ink creation was carried out and it was referred to as comparative example ink CC-7.

[0123]In ink BL-6 of the comparative example 8 [comparative example ink CBL-8] example 6, the ink which used 15 mol of ethylene oxide addition compound of glycerin instead of 15 mol of ethylene oxide addition compound of phenol was created, and it was referred to as comparative example ink CBL-8.

[0124]Each ink of each example and each comparative example was filled up with test-method [regurgitation durability test] 360dpi into the ink-jet recording device which carries the bubble jet recording head which has 64 nozzles via the ink supply tube. The droplet quantity of 4 kHz and a single dot of the drive frequency of a recorder is 80ng. The continuation regurgitation examination of  $5 \times 10^8$  PASURU using 32 nozzles of an every other was carried out on this condition. After the  $5 \times 10^8$  PASURU regurgitation, the judgment printed the document, the poor pattern, and the test document containing a ruled line, respectively, and evaluated degradation of printing nature the first stage. This result was shown in Table 1.

[0125]Evaluation O — a clear character — it is uniform and vivid — poor — Ruled line printing \*\* which prints and gets twisted and which is not — a little blurred character. Poor printing as which the fall of concentration is regarded, ruled line printing [ which \*\*\*\* has generated ] x — The character, uneven and thin poor printing, and the non-regurgitation which it is blurred and are hard to read are also generated, and, in an actual use top problem, disordered ruled line printing O is a level which is not.

[0126][Preservation stability examination] 50 ml of each ink of each example and each comparative example was filled in the shot heat-resistant bottle with a content volume of 100 ml, and was sealed, and the promotion retention test for three months was done at 60 \*\*. The judgment measured after-preservation viscosity and judged the quality of preservability. This result was shown in Table 1.

[0127]Evaluation O — There is almost no viscosity rise and there is also no rise of mean particle diameter.

O — Within 10%, settlings have few viscosity rises to the first stage.

\*\* — \*\*\*\* and precipitation of viscosity change have occurred 10 to 50% to the first stage.

x — It is gelling. Or it is hard precipitation.

O In an actual use top problem, O is a level which is not.

[0128][Textile-printing print test] The color ink JIETO recorder which carries the bubble jet recording head which has 64 nozzles for the ink of Examples 6, 7, and 8 and the comparative examples 4 and 8 by 360dpi was filled up, and color recording was performed to the polyester textile. It heated in steam for 8 minutes at 180 \*\* after record, washing processing of the conventional method was performed, and the textile-printing thing was obtained. The visual judgment was carried out and the level dyeing nature of the obtained textile-printing thing was evaluated. This result was shown in Table 1.

[0129]Evaluation O — There is no coloring nonuniformity of a printed part and it is clear \*\*. — x which there is coloring nonuniformity a little, it got twisted and the blur has generated — The concentration to which it gets twisted and a blur is conspicuous with coloring nonuniformity is

also thin. [0130]

[Table 1]

表 1

	インク	吐出耐久性 試験	保存安定性 試験	捺染プリント テスト
実施例 1	B - 1	○	◎	—
実施例 2	Y - 2	○	◎	
実施例 3	Y - 3	○	◎	
実施例 4	C - 4	○	◎	
実施例 5	M - 5	○	◎	
実施例 6	BL - 6	○	◎	○
実施例 7	R - 7	○	◎	○
実施例 8	Y - 8	○	◎	○
実施例 9	M - 9	○	◎	—
比較例 1	CY - 1	×	◎	—
比較例 2	CY - 2	×	◎	
比較例 3	CC - 3	×	◎	
比較例 4	CBL - 4	×	◎	×
比較例 5	CY - 5	△	△	—
比較例 6	CY - 6	△	×	
比較例 7	CC - 7	×	○	
比較例 8	CBL - 8	△	◎	△

[0131]

[Effect of the Invention]As explained above, the drainage system distribution ink of this invention is the ink for bubble jets which used a disperse dye dispersing element or organic pigment dispersions.

It excels in preservation stability and the stable regurgitation in a bubble jet recorder can be performed.

[0132]According to the drainage system distribution ink of this invention and the ink jet recording method using this, and the recorder, when color recording is performed to a regular paper or textiles, there are not a blot and generating of feathering, and it excels in fixability, and excels in color enhancement, and the good printing quality of robustness is obtained.

[Translation done.]